

Petrolog 4

Manual

Version 4.0.6
February 2024

The latest version of Petrolog and this manual can be downloaded from the Petrolog homepage at:
<https://www.petrologsoftware.com>

Register for updates and new version alerts,
submit your comments and suggestions:
enquiry@petrologsoftware.com

Need help?
support@petrologsoftware.com

Petrolog4 is developed and maintained by *Friendly Solutions*



Friendly Solutions

Technical requirements, installation, and licencing

Petrolog4 runs under Windows operating system (XP or higher). Screen resolution should be set to higher than 1400 x 1000 pixels.

The current release requires a computer with a 64-bit processor. If you require a 32-bit version of the software, please email support@petrologsoftware.com.

Note: Correct display of the main form of Petrolog4 (Fig. 1) may require that the 'Text size' option in Display settings is set to 100% (in earlier versions of Windows, this is the DPI setting that should be set to 'Normal size' at Display Properties/Settings/Advanced/General). To check/change this setting, go to the 'System' section of the Control Panel.

Installation

To instal the software, download Petrolog4.zip file from the website (petrologsoftware.com) and unpack its content into a folder on your computer.

Note: Petrolog would not work correctly if placed in shared/managed folder, i.e., a folder that is administered by OneDrive, Dropbox, Google Drive, or other file sharing software. We suggest making a folder C:\Petrolog4 or C:\Programs\Petrolog4.

Note: Your computer must be connected to the internet when you start Petrolog4 for the first time. Start the program by double-clicking on Petrlog4.exe. When Petrolog4 starts for the first time, the Registration form will open requesting you to enter your Licence Key and User Key (Fig. 1). Once entered,

The screenshot displays the Petrolog 4.0.5 software interface with a registration dialog box open. The background window has a menu bar (File, Export to MS Excel, Tools, Help) and several tabs (Crystallisation, Reverse Crystallisation, Melt Liquidus Association, Olivine MI). It contains multiple panels for inputting data like phase models, extent of fractionation, oxidation state, melt physical properties, and calculation parameters. A 'Starting melt composition' table is also visible. The registration dialog box, titled 'Registration', prompts the user to enter a User Key, Licence Key, Machine Key, Petrolog Version (pre-filled as 4.0.5), Owner, and Expiry Date. It includes 'Ok', 'Reset', and 'Invalid Licence' buttons. At the bottom, it shows the 'Licence state: MustCallIn' and a link to icons. The main window's 'Start calculations' button is visible at the bottom right.

SiO2	TiO2	Al2O3	Fe2O3	FeO	MnO	MgO	CaO	Na2O
50.00	1.00	15.00	0.00	9.00	0.10	10.00	12.00	2.50

Figure 1. The Registration form of Petrolog4 before licence information is entered.

click on the 'Ok' button to start using the software. Once licence is entered, you would not need to return to the Registration until the Licence Key expires. If you open the registration window, you will see your licence information (Fig. 2).

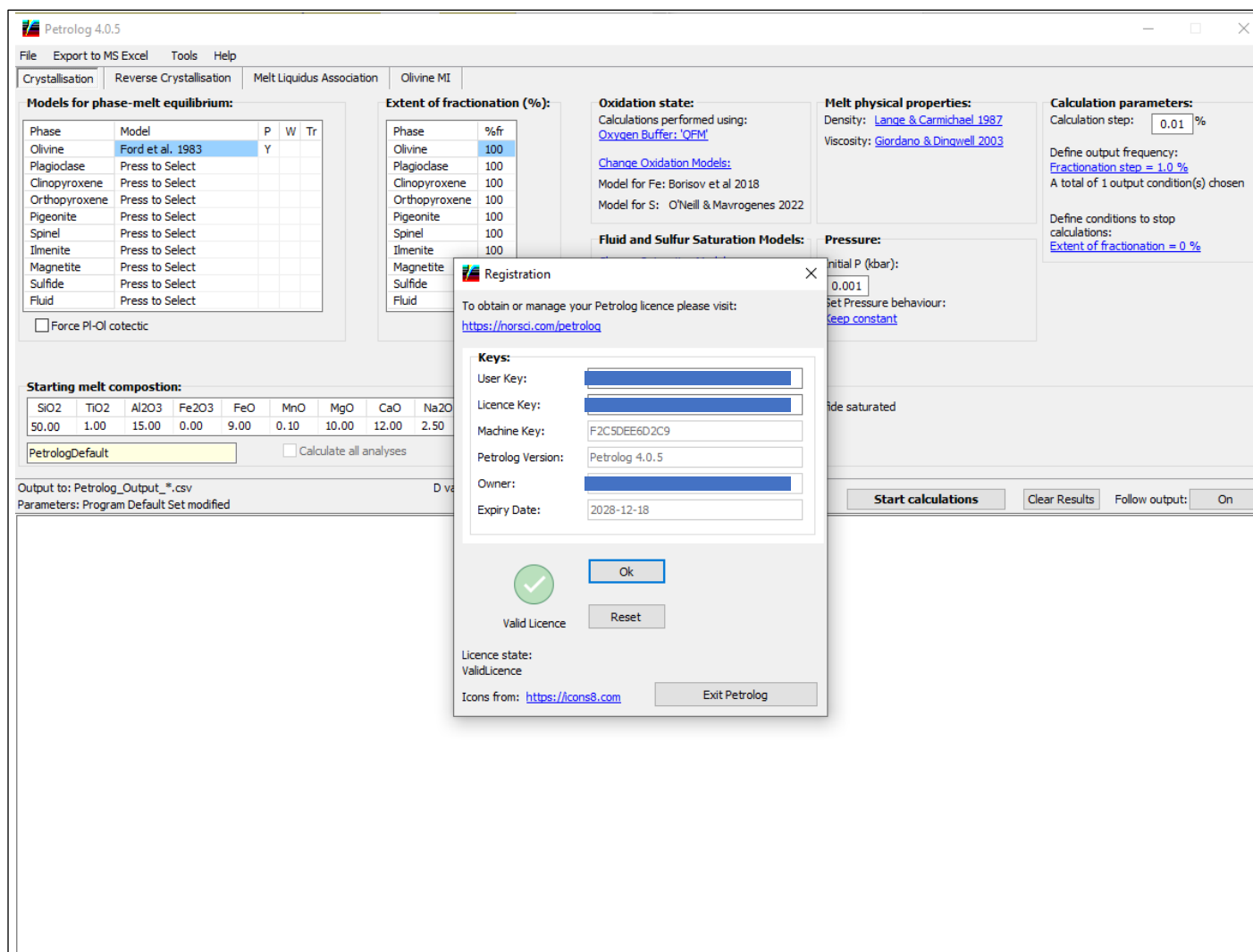


Figure 2. The Registration form of Petrolog4 after licence information is entered.

If you have not purchased your Keys before downloading the software, you can click on the link at the top left corner of the Registration form (<https://norsci.com/petrolog>) that will take you to the webpage where you can register and obtain the Keys.

To close the software without entering the Keys, click on the 'Exit Petrolog' button.

Note: Do not move any individual files unpacked from Petrolog4.zip to other folders on your computer as this would result in a failure to start the program. If you would like to change the folder where Petrolog4 files are stored, copy all unpacked files to the new location.

Licensing

Petrolog4 licences can be purchased for a minimum of 1 year. A single licence can include several installations (licence allocations). The cost of the licence is determined by the number of years it covers and the number of installations it includes. One installation for one year costs AUD\$100 in 2024.

Each Petrolog4 installation is linked to the computer the software is installed on, and the user who installed the software on that computer. More details are provided on <https://norsci.com/?p=user-licences>.

Every time Petrolog4 is started, the program will attempt to connect to the server and validate the licence. If Petrolog4 starts when the computer is off-line, this installation enters an off-line grace period. Each

Petrolog4 licence allocation allows for a 30-day off-line grace period that is counted from the time the program last started when the computer it is installed on was online.

Note: If Petrolog4 have not been run for over 30 days, it will not work if the computer is off-line when the program starts.

Each licence has a 14-day expiration date grace period. If the licence is not renewed within 14 days, Petrolog4 will stop working.

Moving Petrolog4 allocations to a different computer or a different user on the same computer

If you have purchased a licence with a single allocation and would like to change the computer/user you use to run Petrolog4, you would need to logon to your account on norsci.com and deactivate the previous allocation. After that, you will be able to register your available allocation on a different computer and/or under a different user.

1. Overview of Petrolog4

Petrolog4 is software for modelling fractional and equilibrium crystallisation of silicate magmas at variable pressure, melt oxidation state and melt volatile contents.

Other calculation options include modelling reverse of fractional crystallisation and modelling post-entrapment re-equilibration of melt inclusions in olivine.

Modelling of crystallisation in Petrolog4 is based on the concept of pseudo-liquidus temperatures (Nathan, Vankirk, 1978; Nielsen, Dungan, 1983; Ariskin et al., 1986). The method relies on the ability of the mineral-melt equilibrium models to calculate liquidus temperature not only for the range of melt compositions where the minerals are stable, but also for melt compositions outside the stability regions of each mineral (i.e., pseudo-liquidus temperatures).

The essence of the technique is to compare calculated pseudo-liquidus temperatures for a selected set of mineral species that may crystallize from a given melt composition. The mineral with the highest calculated temperature is considered the mineral on the liquidus of the given melt composition. This mineral is subtracted from melt, and then the process is repeated. The algorithm automatically determines the order of appearance of phases on the liquidus of the melt.

Petrolog4 offers a model-independent algorithm, which can incorporate a potentially unlimited number of phase-melt equilibrium models for major and trace elements, of solubility models for fluid components in silicate melts, of melt oxidation state models, and of models describing melt physical parameters such as density and viscosity, and other types of models.

Note: Mineral-melt equilibrium models that can be included in Petrolog4 must calculate both the temperature at which the mineral appears on the liquidus of a given melt composition, and the composition of the mineral, at a given pressure and oxidation state.

Petrolog4 can be used to perform four general types of calculations:

- Modelling Crystallisation,
- Modelling Reverse of Fractional Crystallisation,
- Estimation of Melt Liquidus Association, and
- Modelling Melt Inclusions in Olivine.

Each calculation type can be selected by choosing the appropriate tab from the Main form of the software, which opens when the program is loaded. Four tabs corresponding to the four calculation types above are called 'Crystallisation', 'Reverse Crystallisation', 'Melt Liquidus Association' and 'Olivine MI'.

The 'Crystallisation' tab is shown on Figure 1.1.

Each tab window has three main parts: the top part (grey background) is used for setting the calculation parameters (Parameters Section); the middle part (white background) is used for recording calculation results (Output Section); and the optional bottom part (grey background) is used for recording non-critical debugging messages and warnings (Debug Section).

The Parameters Section has several entry fields and text boxes with white background (e.g., 'Calculation step' or 'Initial pressure'), in which parameter values can be typed in, and several settings in blue, which can be changed by clicking on them and choosing a different setting in a pop-up window.

When parameters are set, calculations are started by pressing the 'Start Calculations' button at the right-hand corner of the Parameters Section. The Output Section will list the set of parameters chosen for calculation and calculation results. Text in the Output Section can be highlighted and copied by pressing Ctrl-C, and then pasted into a text editor.

When calculation starts, the 'Start Calculations' button changes to the 'Interrupt Calculations' button, which can be used to abort the current run.

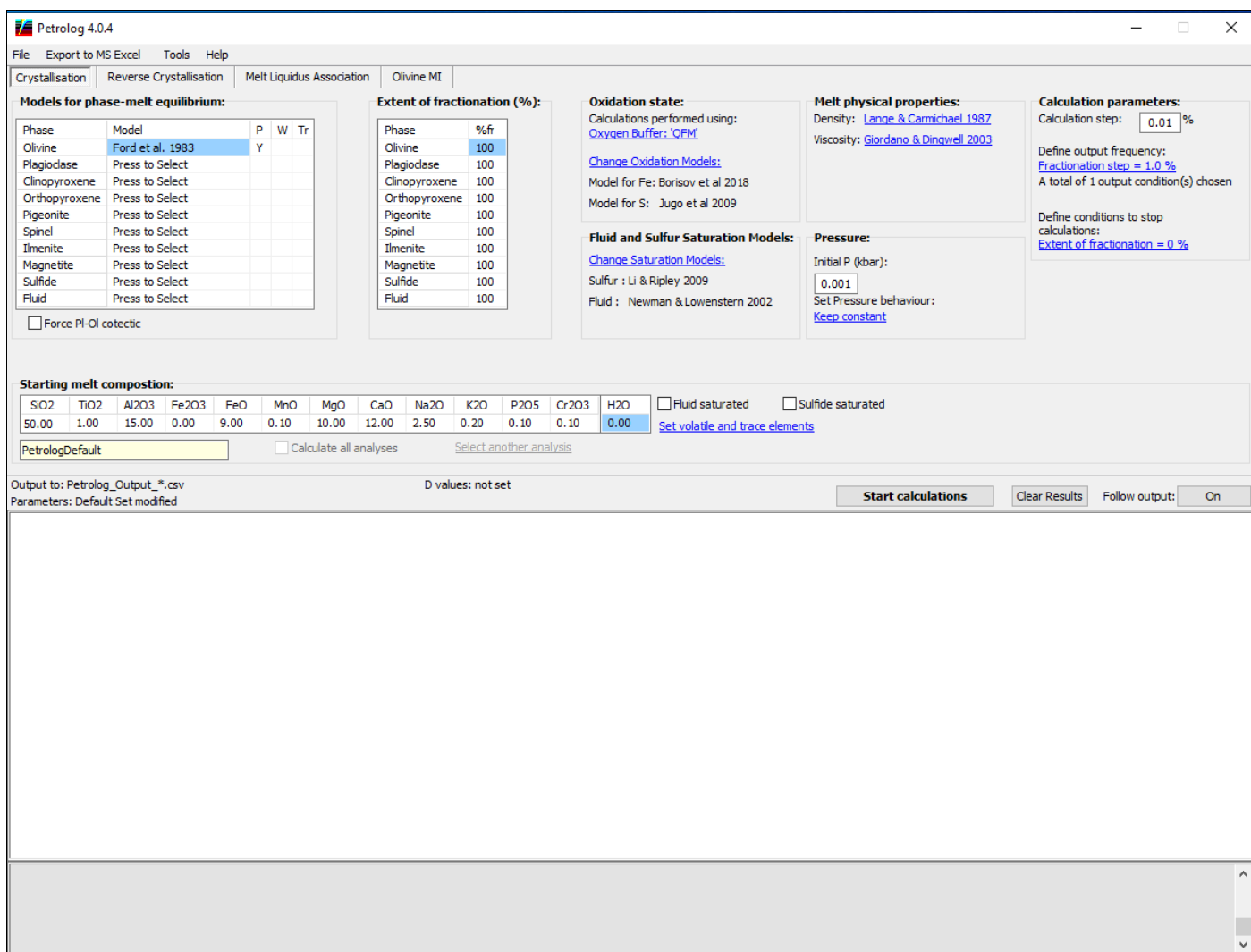


Figure 1.1 'Crystallisation' option of Petrolog4 interface.

The program is loaded with the Program Default Set of parameters and a default starting composition ('PetrologDefault'), and thus pressing the 'Start Calculations' button straight after the program is loaded would result in a default calculation.

Petrolog4.zip contains several recommended predefined sets of parameters for modelling crystallisation of several major geodynamic types of magmas such as mid-ocean ridge basalts and subduction-related magmas. These sets of parameters can also be downloaded from the Petrolog4 website.

Note: It is possible to save a set of parameters as the Default Set that would be loaded automatically every time Petrolog4 starts (see Section 4.2.1 of this manual).

2. Data Input and Output

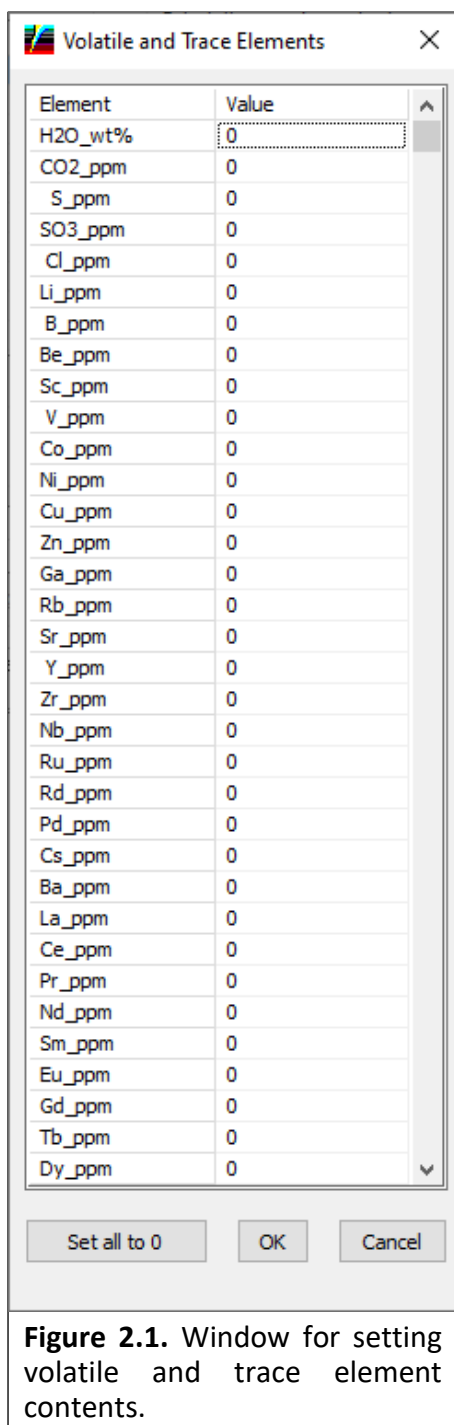
2.1. Defining the Starting composition for calculations

The starting composition is set in the 'Starting Melt Composition' subsection of the Parameters Section (Fig. 1.1). Petrolog4 allows for the starting composition(s) to be entered manually or loaded from a file.

2.1.1. Manual entry of the starting composition.

When the program is loaded, the 'Starting melt composition' subsection of the Parameters Section contains the default starting composition 'PetrologDefault'. This composition can be edited directly within this section. The concentrations of major elements and H₂O are in wt% oxides.

Trace and volatile element contents are set and/or edited by clicking on 'Set volatile and trace elements' label, which opens the 'Volatile and Trace Elements' pop-up window (Fig 2.1).



Element	Value
H2O_wt%	0
CO2_ppm	0
S_ppm	0
SO3_ppm	0
Cl_ppm	0
Li_ppm	0
B_ppm	0
Be_ppm	0
Sc_ppm	0
V_ppm	0
Co_ppm	0
Ni_ppm	0
Cu_ppm	0
Zn_ppm	0
Ga_ppm	0
Rb_ppm	0
Sr_ppm	0
Y_ppm	0
Zr_ppm	0
Nb_ppm	0
Ru_ppm	0
Rd_ppm	0
Pd_ppm	0
Cs_ppm	0
Ba_ppm	0
La_ppm	0
Ce_ppm	0
Pr_ppm	0
Nd_ppm	0
Sm_ppm	0
Eu_ppm	0
Gd_ppm	0
Tb_ppm	0
Dy_ppm	0

Set all to 0 OK Cancel

Figure 2.1. Window for setting volatile and trace element contents.

The concentrations of volatile trace elements of interest are entered into the column 'Value' in ppm (all but H₂O). All elements that have concentrations above zero will be included in calculations. To reset all concentration values to zero press 'Set all to 0' button. Pressing the 'Cancel' button will close the form without applying any changes made.

Note: If concentrations of at least one volatile or trace element are set to a non-0 value, a star (*) appears next to the 'Set volatile and trace elements' label in the 'Starting melt composition' subsection.

2.1.2. Loading starting composition(s) from file.

The starting composition(s) can also be loaded from a file by using the 'Open data file' option in the 'File' menu (Fig. 2.2).

Note: When a file is loaded, its name and full path are displayed at the top of the Petrolog4 main form (Fig. 2.2).

The data file should contain analyses stored as rows with the first row containing element names. The program can read delimited text files that use 'tabs', blank spaces, commas, and semicolons as delimiters. The recognised extensions for file names are '.txt', '.dat' and '.csv'.

Note: The order of elements in the file is not prescribed. Petrolog4 identifies elements by analysing the first row of the data file.

The following abbreviations should be used (not case sensitive): SiO₂, TiO₂, Al₂O₃, Fe₂O₃, FeO, FeO* or FeOt, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅, Cr₂O₃, H₂O, CO₂, S, SO₂, SO₃, Cl, B, Be, Sc, V, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ru, Rd, Pd, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Re, Os, Ir, Pt, Pb, Th, U. The column containing analysis identifiers can be called either 'Name' or 'Sample' or 'Number' or 'Analysis'. Concentrations of major elements and H₂O should be supplied in wt% oxides and for all other elements in ppm. The data file can also contain other columns as described later in this manual.

Note: When both FeO and the total Fe as FeO (FeO* or FeOt) columns are present in the file, the user will be asked to choose whether to load data from the Fe₂O₃ and FeO columns and ignore the total Fe values, or to load the total Fe as FeO and ignore the FeO and Fe₂O₃ values.

Note: Petrolog4 inputs sulphur concentrations as elemental S. The oxidation state of sulphur is determined during calculations based on the magma oxidation state. Sulphur can be entered manually as S or SO₃ or both, or from a datafile as either S, or SO₂, or SO₃ in any

combination. When multiple forms of S are present in the starting composition, the total elemental S content is calculated by summing sulphur entered in different forms.

Note: The starting composition in the ‘Starting melt composition’ subsection does not change during calculations and can be used in subsequent calculations if required.

When a file is loaded, the first analysis in the file is displayed in the ‘Starting melt composition’ subsection. The values in this analysis can be edited in Petrolog4 without affecting the data file stored on disk. When the ‘Start calculations’ button is pressed, the calculations will start using the composition displayed in the ‘Starting melt composition’ subsection.

Petrolog 4.0.4 Input from: C:\Programs\PETROLOG\Current_data_File.csv

File Export to MS Excel Tools Help

Open Data File
File for output...
Save Parameters
Load Parameters
Save Parameters as the Default Set
Load the Default Set of Parameters
Exit...

Melt Liquidus Association Olivine MI

Extent of fractionation (%):

Phase	%fr
Olivine	80
Plagioclase	50
Clinopyroxene	70
Orthopyroxene	70
Pigeonite	70
Spinel	0
Ilmenite	0
Magnetite	0
Sulfide	100
Fluid	100

Oxidation state:
Calculations performed using:
Oxygen Buffer: 'QFM'
Change Oxidation Models:
Model for Fe: Borisov et al 2018
Model for S: Jugo 2009

Melt physical properties:
Density: Lange & Carmichael 1987
Viscosity: Giordano & Dingwell 2003

Calculation parameters:
Calculation step: 0.01 %
Define output frequency:
Fractionation step = 1.0 %
A total of 1 output condition(s) chosen
Define conditions to stop calculations:
Extent of fractionation = 70 %

Fluid and Sulfur Saturation Models:
Change Saturation Models:
Sulfur: Li & Ripley 2009
Fluid: Newman & Lowenstern 2002

Pressure:
Initial P (kbar): 5
Set Pressure behaviour: dP/dF

Starting melt composition:

SiO2	TiO2	Al2O3	Fe2O3	FeO	MnO	MgO	CaO	Na2O	K2O	P2O5	Cr2O3	H2O
48.00	1.00	14.00	0.50	9.00	0.16	7.00	9.00	2.00	0.20	0.22	0.08	0.00

Analysis1 ☐ Calculate all analyses [Select another analysis](#)

Output to: Petrolog_Output_*.csv
Parameters: last loaded from Current_Param.PtlParam modified
D values: loaded from Current_D_set.PtlDSet

Start calculations Clear Results Follow output: On

Figure 2.2. The main form of Petrolog4 with the content of the File Menu shown. The name of the loaded data file with the starting compositions is displayed at the top of the form. The name of the loaded file with calculations parameters (if loaded) is displayed above the Output window on the left side of the form. The name of the file with distribution coefficients for trace and volatile elements (D values), if loaded, is displayed above the Output window in the centre of the form. The name of the file for saving the result is displayed above the Output window on the left side of the form.

If the data file contains more than one analysis, it is possible to choose another analysis by clicking on the ‘Select another analysis’ label in the ‘Starting melt composition’ subsection. In the pop-up window that appears (Fig. 2.3), double-click on the analysis to choose it. This will close the window and return to the main form. The concentration values for the chosen analysis will appear in the ‘Starting melt composition’ subsection of the main form. To close the ‘Select analysis’ window without choosing an analysis, click on the cross in the top right corner.

Analysis Number	SiO2	TiO2	Al2O3	Fe2O3	FeO	MnO	MgO	CaO	Na2O	K2O	P2O5	Cr2O3	H2O_w	CO2_p	S_ppm	Cl_ppm	Co_ppm	Ni_ppm	Rb_ppm	Sr_ppm	Ba
Analysis1	48	1	14	0.5	9	0.16	7	9	2	0.2	0.22	0.08	0	0	2000	68	60	92	10	226	61
Analysis2	51	1.3	16	1	8	0.18	11	10	1.7	0.7	0.11	0.11	0.5	0	0	61	55	73	9	86	68
Analysis3	48	0.8	14	0.6	11	0.2	9	13	2	0.6	0.24	0.13	0	0	200	36	50	88	15	54	55
Analysis4	48	1.3	13	0.9	8	0.23	7	10	2.4	1.6	0.18	0.13	0	0	0	23	56	144	3	200	83
Analysis5	50	1	15	0.8	11	0.21	10	11	2.5	0.3	0.2	0.14	0	0	0	29	41	290	3	87	89
Analysis6	47	0.6	17	1	11	0.2	9	10	2.1	2	0.09	0.23	0	0	0	60	60	138	7	100	46
Analysis7	50	0.5	17	1	9	0.14	10	12	3.1	1.9	0.1	0.16	0	0	0	39	34	150	18	272	90
Analysis8	47	1.4	15	0.6	11	0.17	12	9	2	1	0.14	0.21	0	0	0	65	70	147	4	172	57
Analysis9	52	1.5	17	0.5	9	0.21	9	8	2.6	0.8	0.11	0.24	0	0	0	95	30	164	12	68	86
Analysis10	48	1.2	14	0.5	11	0.2	10	10	3.2	1.7	0.19	0.16	0	0	0	51	47	93	18	42	64
Analysis11	49	0.6	14	0.9	9	0.11	11	9	1.6	1.6	0.07	0.13	0	0	0	99	42	104	5	145	95
Analysis12	48	1.1	14	0.7	11	0.17	8	8	2.7	1.9	0.08	0.12	0	0	0	58	63	196	18	258	63

Figure 2.3. Window for selecting an analysis from the imported datafile.

2.1.2.1. Calculating multiple analyses from the loaded data file

Petrolog4 offers an option of calculating all analyses in the data file using the same set of calculation parameters. The data file can also contain columns that store parameters for stopping calculations for each analysis (see section 4.1.8 for details).

When a data file is loaded, the 'Calculate all analyses' check box becomes active (Fig. 2.2) if there is more than one analysis in the file.

Note: When the 'Calculate all analyses' box is checked, Petrolog4 ignores the composition in the 'Starting melt composition' subsection, and instead reads consequently analyses from the loaded data file.

2.2. Saving the results of calculations to a file

Petrolog4 offers three options for saving calculation results for future use.

I. During calculations, Petrolog4 continuously prints the state of the system into the Output Section of the Main Form (Fig. 1.1). This output can be highlighted within the Output Section by first clicking inside the section and pressing Ctrl+A, and then copied (Ctrl+C) to the clipboard pasted into a text editor.

II. Petrolog4 can save the output into a number of comma-separated values files (.csv) with a user specified name.

To specify the file name for the file into which calculation results will be saved, use the 'File for output...' option in the 'File' section of the Main Menu on the main form (Fig. 2.2). Type in the desired file name into the 'File name:' field on the 'Save As' dialog form that opens, choose the folder for saving the file, and press the 'Save' button. Do not provide an extension for the file name as it will be ignored.

A general form of the file names generated by Petrolog4 is 'UserSpecifiedName_*.csv'. The user-specified file name is displayed above the Output window on the left side of the Main form (Figs. 1.1, 2.2). The number of files created by Petrolog4, and their structure, depend on the chosen calculation option and will be described later on in this manual.

Note: Output files saved during modelling crystallisation calculations have 'FRAC' added to the user-specified name (i.e., 'UserSpecifiedName_FRAC_*.csv'). Output files saved during modelling reverse of fractional crystallisation calculations have 'REV' added to the user-specified name. Output files saved during estimation of melt liquidus association calculations have 'MLA' added to the user-specified name. Output files saved during modelling melt inclusions in olivine have either 'IRL' or 'PIC' or 'PCR' added to the user-specified name, depending on the chosen type of calculations.

After the calculations are completed, the saved files can either be opened manually or can be exported into Excel (recommended) by using the 'Export to MS Excel' section of the Main Menu (Figs. 1.1, 2.2). The latter creates an Excel workbook with several worksheets containing all the details of the calculation.

Choose either the 'Results of previous calculations' or 'Results of the last calculation'. When exporting results of a previous calculation, a dialog window pops-up where the user should select the file to open. Results of the last calculations are exported automatically.

Note: If the user-specified file name is not changed before starting the next calculation, results of the previous calculation saved in the .csv files would be overwritten.

III. If a user specified name is not provided, Petrolog4 saves the results into .csv files named 'Petrolog_output' instead of 'UserSpecifiedName'. These files can be opened in the same way as described above. Since in this case every calculation produces files with the same name, they are overridden at the beginning of calculation.

2.3. Reading data files and saving the results of calculations when using non-English language versions of Windows

Petrolog4 allows the user to choose the decimal separator and the delimiter for the comma-delimited-values text files (*.csv). The default settings are '.' for the decimal separator and ',' for the *.csv delimiter, that are default settings for English language version of Windows. The user can change the separator to ';' and the delimiter to ';' in the Petrolog Options form (Fig. 2.4) that can be displayed by choosing the 'Options' item in the 'Tools' section of the Main Menu.

Note: These settings only affect the format of files read and written by Petrolog4. They have no effect on the display of numbers within the software.

Petrolog 4.0.6 Memory Usage: 1.425 Mb

File Export to MS Excel Tools Help

Crystallisation Reverse Crystallisation Melt Liquidus Association Olivine MI

Models for phase-melt equilibrium:

Phase	Model	P	W	Tr
Olivine	Ford et al. 1983		Y	
Plagioclase	Press to Select			
Clinopyroxene	Press to Select			
Orthopyroxene	Press to Select			
Pigeonite	Press to Select			
Spinel	Press to Select			
Ilmenite	Press to Select			
Magnetite	Press to Select			
Sulfide	Press to Select			
Fluid	Press to Select			

☐ Force Pl-Ol cotectic

Extent of fractionation (%):

Phase	%fr
Olivine	100
Plagioclase	100
Clinopyroxene	100
Orthopyroxene	100
Pigeonite	100
Spinel	100
Ilmenite	100
Magnetite	
Sulfide	
Fluid	

Oxidation state:
Calculations performed using:
[Oxygen Buffer: 'QFM'](#)
[Change Oxidation Models:](#)
Model for Fe: Borisov et al 2018
Model for S: O'Neill & Mavrogenes 2002

Fluid and Sulfur Saturation Models:

Melt physical properties:
Density: [Lange & Carmichael 1987](#)
Viscosity: [Giordano & Dingwell 2003](#)

Calculation parameters:
Calculation step: 0.01 %
Define output frequency:
[Fractionation step = 1.0 %](#)
A total of 1 output condition(s) chosen
Define conditions to stop calculations:
[Extent of fractionation = 0 %](#)

Starting melt composition:

SiO2	TiO2	Al2O3	Fe2O3	FeO	MnO	MgO	CaO	N
50.00	1.00	15.00	0.00	9.00	0.10	10.00	12.00	2

PetrologDefault ☐ Calculate all analyses

Output to: Petrolog_Output_*.csv
Parameters: Program Default Set

Petrolog Options

☒ Save Data File Name with Parameters
☒ Save Os File Name with Parameters
☐ CSV files delimiter (; for some non-English Windows versions)
☐ Decimal Separator (, for some non-English Windows versions)
QFM Reference Oxygen Buffer for lg(fO2) output

OK Cancel

Start calculations **Clear Results** Follow output: On

Figure 2.4. Petrolog Options form is opened by selecting the 'Options' item in the 'Tools' section of the Main Menu. Note that the Debug Section at the bottom of the Main Form is not displayed on this example as Debug output has been switched off by using the 'DebugOutput On/Off' item in the 'Tools' section of the Main Menu.

3. Defining and storing sets of values of distribution coefficients (D) for trace and volatile elements

In general, $D_{\text{phase}}^i = C_{\text{phase}}^i / C_{\text{melt}}^i$, where ' C^i ' are concentrations of element ' i ' in a phase (e.g., plagioclase, fluid, sulphide melt, etc.) and in the silicate melt.

Petrolog4 provides three approaches to handling distribution coefficients (D).

I. Some of the phase-melt equilibrium models incorporate some trace and volatile elements. When such models are chosen for calculations, by default the concentrations of these elements in the phase will be calculated following the approach used in the model (e.g., the model of Herzberg and O'Hara, 2002 for olivine melt-equilibrium incorporates Ni).

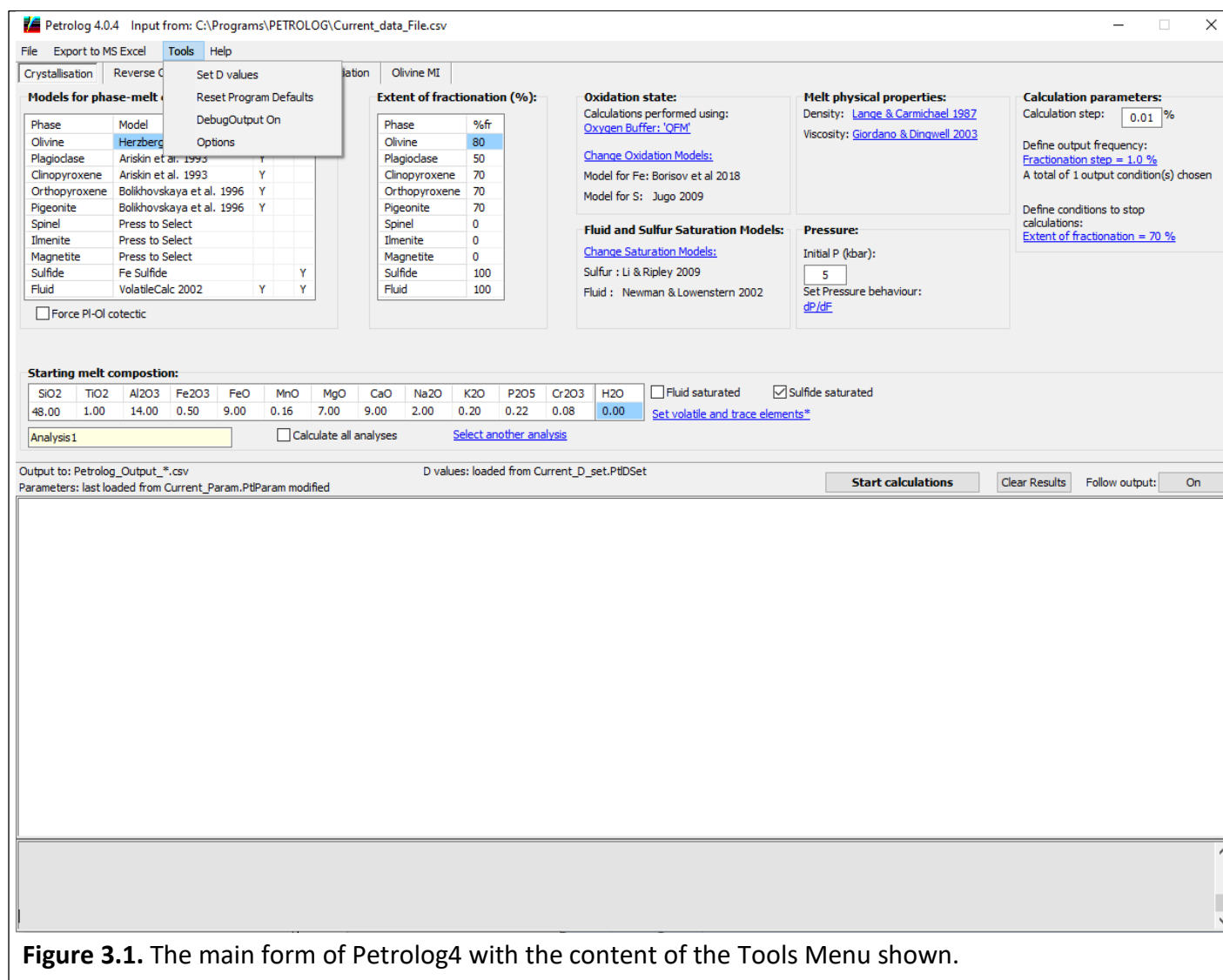


Figure 3.1. The main form of Petrolog4 with the content of the Tools Menu shown.

II. One can set a constant D value, which is then used in the calculation(s).

To enter D values, use the 'Set D values' option in the 'Tools' menu (Fig. 3.1). A pop-up window 'Set D Values' appears (Fig. 3.2).

Constant D values for any phase/element can be set by entering them into the corresponding cells (Fig. 3.2). The entered D values must be calculated using weight units of concentration.

If any of the currently chosen models of phase-melt equilibrium incorporate volatile or trace elements, these models will be displayed in the corresponding cells on the form. For the example shown on Figure 3.2, VolatileCalc model (Newman and Lowenstern, 2002) is chosen for fluid-melt equilibrium, pure FeS model is chosen for sulphide-melt – silicate-melt equilibrium, and Herzberg and O'Hara (2002) model is chosen for

olivine-melt equilibrium. As a result, 'Herzb02' is displayed in the Ni cell for olivine, 'FeS' is displayed for the S cell for sulphide, and 'VltlCalc' is displayed in the H₂O and CO₂ cells for fluid.

Element	Olv	Plg	Cpx	Opx	Pig	Spl	Ilm	Mgt	Sil	Fld
H2O	0	0	0	0	0	0	0	0	0.1	VltlCalc
CO2	0	0	0	0	0	0	0	0	0	VltlCalc
S	0	0	0	0	0	1			FeS	0
SO3	0	0	0	0	0	0			0	0.2
Cl	0	0	0.001	0.001	0.01	0			0	0.05
Li	0.02	0.02	0.01	0	0	0			0	0
B	0	0	0	0	0	0			0	0
Be	0	0	0	0	0	0			0	0
Sc	0	0	0	0	0	0			0	0
V	0	0	0	0	0	0			0	0
Co	Beatt91	0	0.2	0.8	0.8	0			0	0
Ni	Herzb02	0	1	1.5	1.2	0			10	0
Cu	0	0	0	0	0	0			0	0
Zn	0	0	0	0	0	0			0	0
Ga	0	0	0	0	0	0	0	0	0	0
Rb	0.001	0.1	0.05	0.02	0.03	0	0	0	0	0.2
Sr	0.01	Bl_Wo91	0.07	0.05	0.05	0	0	0	0	0.2
Y	0	0	0	0	0	0	0	0	0	0
Zr	0	0	0	0	0	0	0	0	0	0
Nb	0	0	0	0	0	0	0	0	0	0
Ru	0	0	0	0	0	0	0	0	0	0
Rd	0	0	0	0	0	0	0	0	0	0
Pd	0	0	0	0	0	0	0	0	0	0
Cs	0	0	0	0	0	0	0	0	0	0
Ba	0	Bl_Wo91	0.03	0.015	0.02	0	0	0	0	0.3
La	0	0	0	0	0	0	0	0	0	0
Ce	0	0	0	0	0	0	0	0	0	0
Pr	0	0	0	0	0	0	0	0	0	0
Nd	0	0	0	0	0	0	0	0	0	0

Buttons: Set all Ds to 0, Load a set of Ds from file, Save this set of Ds, OK, Cancel

Figure 3.2. Form for defining D values to be used in calculations. If a model for D values for an element in a phase is available, a popup window will appear in the middle of the form, as shown for Sr in plagioclase. See text for details.

Note: If desired, the displayed model names can be overwritten by a constant D value by entering the value in the corresponding cell.

III. Petrolog4 allows for using models that define D values for an element in a phase as a function of various parameters, such as melt composition, temperature, phase composition, etc. If D models are available for an element in a phase, a pop-up window will appear when clicking on the cell for that element/phase (Fig. 3.2). The pop-up window will display all available models for the element in the phase. All elements available in the model are listed (e.g., Ba and Sr are available in the Blundy and Wood, 1991 model for plagioclase, Fig. 3.2). Clicking on the list of elements (not the name of the model) will apply the model to the selected element. If the 'Set for all elements' checkbox is ticked before selecting a model, the model will be applied for all elements, not just the one that was clicked on the form. If required, D values for individual elements in the list can be later set to constant values by entering the D value into the 'Set D Value:' box and pressing the 'Close panel' button. This will not affect the application of the chosen model to the remaining elements in the list.

Note: The pop-up window only appears when clicking on an element for which a D model is available. The pop-up window disappears after clicking on a cell for an element for which no D models are available in Petrolog.

D models available in the current version of Petrolog4 are listed in Appendix 1.

Note: Petrolog assigns a charge of +4 to the oxidised sulphur in the fluid. In all other phases, the charge of oxidised sulphur is +6. Thus, the D value for oxidised sulphur between the fluid and silicate melt is defined as $C^{SO_2}_{fluid} / C^{SO_3}_{melt}$.

To save the chosen set of D values and models, press the 'Save this set of Ds' button. In the dialog form that appears, enter a file name and press Save.

Note: Petrolog4 assigns .PtIDSet extension to files with D values.

To load a saved set of D values, press the 'Load a set of Ds from file' button, chose the file in the dialog window, and press Open.

To finish editing D values, close the form by pressing the 'Ok' button. To close the form without applying any of the changes, press the 'Cancel' button.

4. Modelling crystallisation

To model crystallisation, chose 'Crystallisation' tab of the Main form (Figs. 1.1, 2.2, 3.1).

4.1. Setting calculation parameters

The following calculation parameters can be set before starting calculations:

- 1) set of phases involved in calculations;
- 2) phase-melt equilibrium model for each phase;
- 3) extent of fractionation for each phase;
- 4) melt oxidation state;
- 5) fluid and sulphur saturation models;
- 6) pressure;
- 7) melt density and viscosity models;
- 8) calculation step;
- 9) conditions for stopping calculations;
- 10) conditions for the output of results during calculation.

These are described in detail below.

Note: Petrolog4.zip file contains recommended predefined sets of parameters for modelling crystallisation of several major geodynamic types of magmas such as mid-ocean ridge basalts and subduction-related magmas. These sets of parameters can also be downloaded from the Petrolog4 website.

4.1.1. Choosing phases and phase-melt equilibrium models

Minerals and models are chosen in the 'Models for phase-melt equilibrium' subsection of the Parameters Section (Figs. 1.1, 3.1).

When 'Press to Select' is written in the 'Model' field next to a phase name when 'Start calculations' button is pressed, this phase will not be included in calculations. If a model abbreviation is written next to a phase name (e.g., Ford et al., 1983 next to Olivine on Fig. 1.1), the phase will be included in calculations.

Note: Selecting a phase for calculations does not guarantee that it will appear on the liquidus during calculations. Petrolog4 algorithm determines the order of crystallisation based on the chosen parameters.

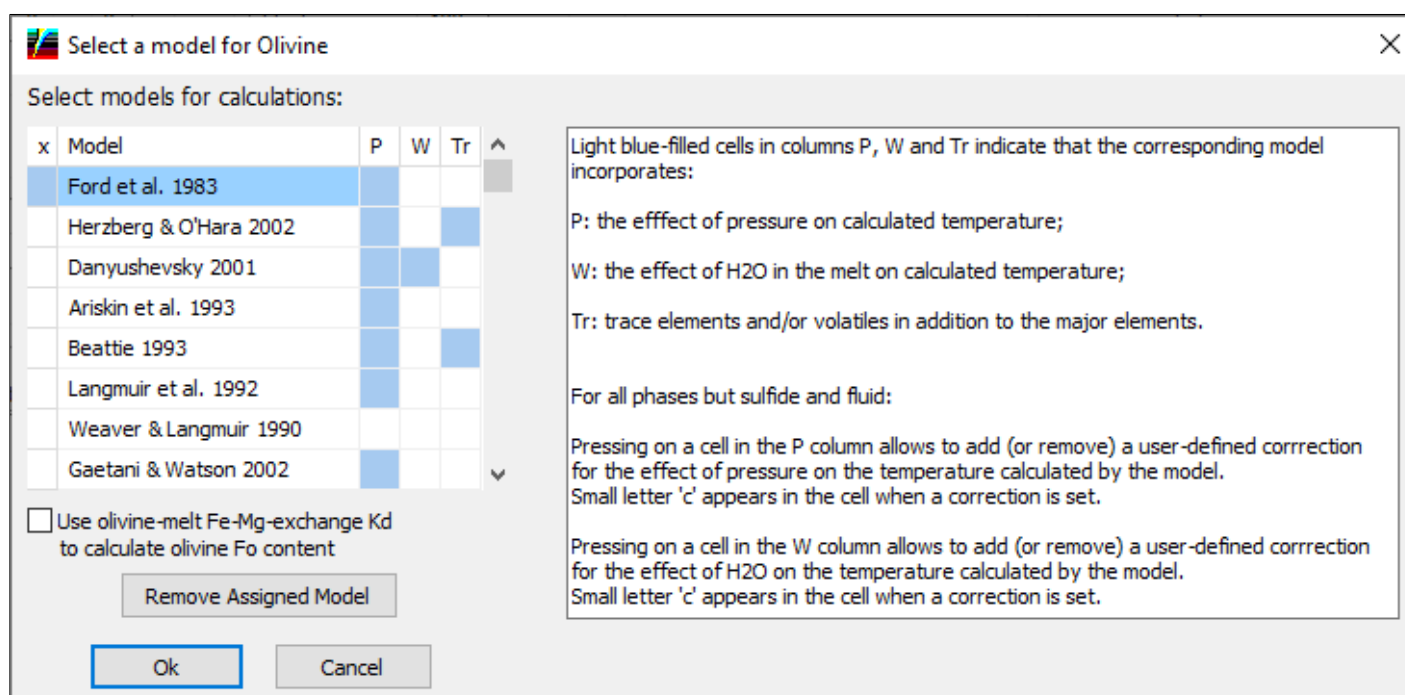


Figure 4.1. Window for choosing an olivine-melt model to be used in calculations.

To choose a model for a phase, click on the 'Model' field for that phase. A pop-up window with a list of available models for this phase will appear (Fig. 4.1).

This window contains a table with 4 columns. Text box on the right provides a brief explanation on how to use the form and interpret the information shown on the form.

Column 'Model' lists model abbreviations.

Column 'P' indicates whether a model incorporates the effect of pressure on the phase-melt equilibrium (the cell is coloured light blue), or alternatively it is designed for the atmospheric pressure only (the cell has white background) (Fig. 4.1).

Column 'W' indicates whether a model incorporates the effect of H₂O on phase -melt equilibrium (the cell is coloured light blue), or alternatively it is designed for anhydrous conditions only (the cell has white background) (Fig. 4.1).

Column 'Tr' indicates whether a model incorporates any trace or volatile elements. If the 'Tr' cell for a model is coloured light blue, the model incorporates some of those elements. (Fig. 4.1).

Blue rectangle to the left of the Ford et al. (1983) cell (Fig. 4.1) indicates that this model is currently chosen for calculations.

Clicking on the name of a different model will change selection to that model.

Clicking on the 'Remove Assigned Model' button will deselect the selected model and not select any other model (Fig. 4.2). Clicking on the 'Ok' button when no model is selected will result in 'Press to Select' showing next to the phase in the 'Models for phase-melt equilibrium' subsection of the main form (Figs. 1.1, 2.2, 3.1).

Clicking on the 'Cancel' button will close the form without applying any of the changes made.

When choosing a model for olivine-melt equilibrium, the 'Use olivine-melt Fe-Mg-exchange Kd to calculate olivine Fo content' check box at the bottom of the form can be used to set an olivine-melt Fe-Mg exchange Kd value for calculation of olivine composition. This calculated composition will be used instead of the composition calculated by the selected olivine-melt model.

Note: When no model is selected, the 'Use olivine-melt Fe-Mg-exchange Kd to calculate olivine Fo content' check box is disabled.

When the box is checked, a pop-up window appears that is used to determine how the Kd values are determined (Fig. 4.3). Four options are available for calculating Kd values:

Four options are available for calculating Kd values:

'Kd = const': When this option is chosen, a Kd value must be entered in the box to the right, that will be used in calculations.

' $\ln(Kd) = A/T(K)+B*P(kbar)/T(K)+C$ ': When this option is chosen, values for coefficients A, B and C must be provided. The default values correspond to a Kd value of 0.3.

'Sobolev & Danyushevsky 1994': When this option is chosen, Kd values will be calculated following the method described in the Appendix 1 of Sobolev and Danyushevsky (1994).

‘Toplis 2005’: When this option is chosen, Kd values will be calculated using the method of Toplis (2005).

Note: When calculating olivine compositions using a Kd value, the olivine-melt equilibrium model chosen in the ‘Select a model for Olivine’ window (Fig. 4.2) is used for calculating olivine crystallisation temperature, whereas olivine composition is calculated using the specified Kd value or model.

Pressing the ‘Cancel’ button will close the form without applying any of the changes made.

To deselect the Kd option on the ‘Select a model for Olivine’ window (Fig. 4.2), uncheck the ‘Use olivine-melt Fe-Mg-exchange Kd to calculate olivine Fo content’ box by clicking on it when it is checked.

To set a model for another phase, click on the ‘Model’ field for that phase in the ‘Models for phase-melt equilibrium’ subsection of the Parameters Section (Figs. 1.1, 2.2, 3.1).

Note: The available models for sulphide and fluid calculate the compositions of these phases for the given pressure, temperature and melt composition. Thus, including these models in calculations requires choosing at least one silicate or oxide mineral-melt model to enable temperature calculations. Oxidised sulphur is assumed to have a charge of +4 in the fluid phase and +6 in all other phases.

Note: When either H₂O or CO₂ are present in the starting composition, the user must choose a model for fluid-melt equilibrium before starting calculations. When S is present in the starting composition, the user must choose a sulphide melt – silicate melt equilibrium model before starting calculations.

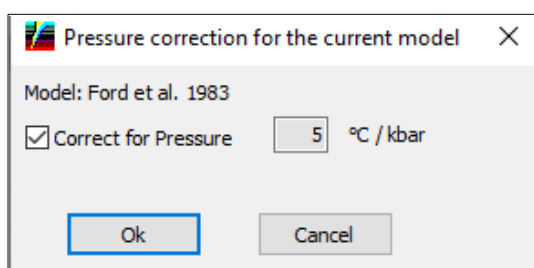


Figure 4.4. Window for setting a correction for the effect of pressure on the calculated liquidus temperature.

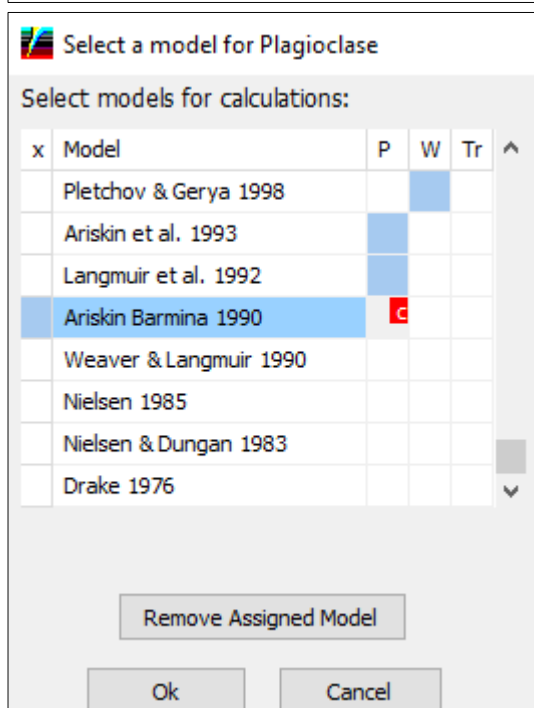


Figure 4.5. Window for choosing a model for plagioclase-melt equilibrium with ‘c’ in column ‘P’ next to the chosen model indicating that a pressure correction is set.

4.1.1.1. Setting a pressure correction to the temperature calculated by the chosen model

Petrolog4 offers an option to introduce a user-defined linear correction for the effect of pressure on crystallisation (liquidus) temperature calculated by a model. A separate correction value can be set for of each mineral involved in calculations. To set a correction, click on the ‘P’ cell next to the chosen model. This opens a pop-up window where a correction value in degrees/kbar can be set (Fig. 4.4).

Pressing the ‘Cancel’ button will close the form without applying any changes.

When correction is set, small letter ‘c’ on red background appears in the ‘P’ cell next to the chosen model (Fig. 4.5).

Note: Since sulphide melt and fluid models do not calculate crystallisation temperatures, a pressure correction cannot be set for these phases.

Note: If the ‘Ok’ button is clicked when the correction value is 0, no correction is applied, even if the ‘Correct for Pressure’ checkbox is checked.

Note: When correction is set, it is applied to the temperature calculated by the chosen model regardless of whether the chosen model incorporates pressure or not.

Note: Once chosen, a correction, applies to all models, i.e., if the phase-melt model is changed after the correction is set, the correction will apply automatically to the new model. To remove the correction, open the ‘Pressure correction’ window again (Fig. 4.4) and uncheck the ‘Correct for Pressure’ box. The small letter ‘c’ in the ‘P’ cell will disappear returning the form to its original state (e.g., Fig. 4.2).

Note: Setting a user-defined correction for the effect of pressure on the liquidus temperature, does not affect the mineral composition that the chosen model calculates.

4.1.1.2. Setting an H₂O correction to the temperature calculated by the chosen model

As only a few models available in Petrolog4 incorporate the effect of melt H₂O content on crystallisation temperature and/or composition of crystallizing phases (e.g., Plechov and Gerya, 1998; Danyushevsky, 2001; Putirka, 2005), Petrolog4 allows the user to introduce corrections to the ‘anhydrous’ models for the effect of H₂O on crystallisation temperatures, to enable calculations under hydrous conditions using models developed for anhydrous conditions only.

To set a correction, click on the ‘W’ cell next to the chosen model (Figs. 4.2, 4.5). This opens a pop-up window ‘Temperature correction for melt H₂O content’ (Fig. 4.6) which is used to set the correction.

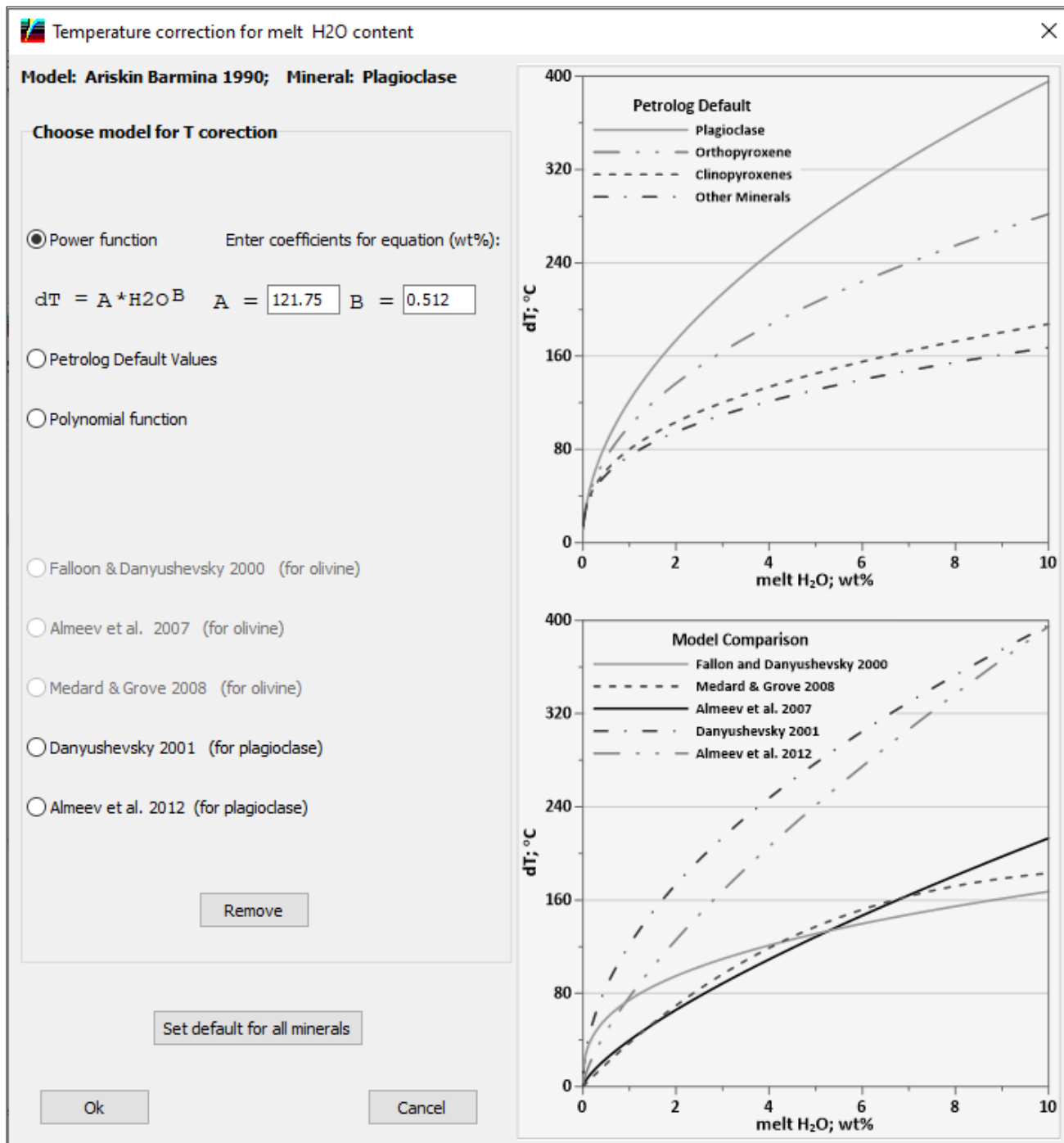


Figure 4.6. Window for setting a correction for the effect of H₂O on liquidus temperature of plagioclase.

Note: Similarly to the pressure correction described above, applying an H₂O correction to the calculated temperature does not affect the calculated phase compositions. Also similarly to the pressure correction, an H₂O correction cannot be set for sulphide melt and fluid models.

Note: When correction is set, it is applied to the temperature calculated by the chosen model regardless of whether the chosen model incorporates H₂O or not.

Petrolog4 offers several options for setting an H₂O correction: user defined power or polynomial functions, Petrolog4 default corrections, and published models for setting H₂O correction that are currently available for olivine and plagioclase only. Petrolog4 default corrections are plotted on the top graph on the form. A comparison between published models is plotted on the bottom plot on the form. The list of available models for H₂O corrections is presented in Appendix 1.

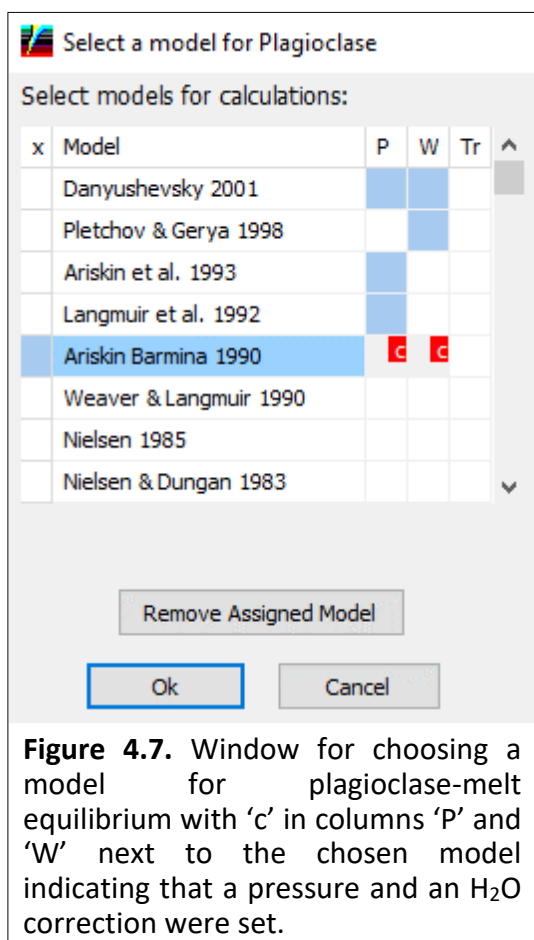
Petrolog4 default corrections (Fig. 4.6) are power functions $dT\ (^{\circ}C) = A * (H_2O\ wt\%)^B$ with the following coefficients:

plagioclase:	A = 121.75	B = 0.512
orthopyroxene:	A = 100.0	B = 0.45
clinopyroxenes:	A = 90.0	B = 0.37
olivine and oxides:	A = 74.404	B = 0.352

A polynomial correction can be set in a form: $dT\ (^{\circ}C) = A * (H_2O\ wt\%)^3 + B * (H_2O\ wt\%)^2 + C * (H_2O\ wt\%)$.

Note: if desired, a linear correction can be set by using either power or polynomial corrections and setting B to 1 for the former or setting A and B to 0 for the latter.

When correction is set, small letter 'c' on red background appears in the 'W' cell next to the chosen model (Fig. 4.7).



Models for phase-melt equilibrium:

Phase	Model	P	W	Tr
Olivine	Herzberg & O'Hara 2002	Y		Y
Plagioclase	Ariskin Barmina 1990	c	c	
Clinopyroxene	Langmuir et al. 1992	Yc	c	
Orthopyroxene	Bolikhovskaya et al. 1996	Y		
Pigeonite	Bolikhovskaya et al. 1996	Y		
Spinel	Press to Select			
Ilmenite	Press to Select			
Magnetite	Press to Select			
Sulfide	Fe Sulfide			Y
Fluid	VolatileCalc 2002	Y		Y

☐ Force Pl-Ol cotectic

Figure 4.8. The 'Models for phase-melt equilibrium' subsection of the Parameters Section showing selected mineral-melt models; whether the selected models incorporate pressure, H₂O and trace elements ('Y'); and which models have corrections set for the effects of pressure and H₂O ('c').

Note: Once chosen, a correction, applies to all models, i.e., if the phase-melt model is changed after the correction is set, the correction will apply automatically to the new model. To remove the correction, open the 'Temperature correction for melt H₂O content' window again (Fig. 4.6) and press 'Remove' button. The small letter 'c' in the 'W' cell will disappear returning the form to its original state (e.g., Fig. 4.2).

The 'Mineral-melt models' subsection of the Parameters Section (Fig. 1.1) display the models chosen for each mineral and uses columns 'P', 'W', and 'Tr' to indicate whether the chosen models incorporate effects of pressure and/or H₂O, and/or trace elements, and whether any user-defined correction are set for the effects of pressure and melt H₂O contents. Capital 'Y' is used to indicate that a model includes a corresponding effect, whereas 'c' is used to indicate that a correction is set (Fig. 4.8).

4.1.1.3. Calculating an olivine - plagioclase \pm clinopyroxene cotectic crystallisation.

Petrolog4 offers an option of forcing the starting composition on an olivine-plagioclase (+/- clinopyroxene) cotectic by adjusting melt H₂O content, following the method of Danyushevsky (2001). The essence of the approach is to first calculate the amount of H₂O which is required for the starting composition to lie on an olivine-plagioclase cotectic, and then to model crystallisation with this H₂O content in the starting composition, so that the composition is cotectic from the onset of crystallisation. (see Danyushevsky, 2001 for a detailed description of the approach). The set of minerals is limited to olivine, plagioclase and clinopyroxene, and the set of models is limited to those from Danyushevsky (2001).

To use this option, check the 'Force Pl-Ol cotectic' checkbox in the 'Models for phase-melt equilibrium' subsection of the Parameters Section (Fig. 4.8).

Note: This option should be used for MORB and BABB compositions only, as the models of Danyushevsky (2001) have not been calibrated outside that compositional range.

Note: When using this option, calculation pressure should be set at a value that ensures that the melt H₂O content required is less than the saturation value (see section 4.1.4).

4.1.2. Setting extent of fractionation for each phase

Petrolog4 allows for a specific extent of fractionation to be set for each mineral using the 'Extent of fractionation (%)' subsection of the Parameters Section (Figs. 1.1, 2.2, 3.1). By default, a value of 100% is assigned to each phase, corresponding to the case of pure fractional crystallisation. When modelling pure fractional crystallisation, a phase is 'removed' from contact with melt and placed into the 'cumulate' part of the system, thus retaining its original composition.

If 0% is assigned to a phase, this corresponds to pure equilibrium crystallisation. When modelling equilibrium crystallisation, the total amount of the crystallized phase remains in equilibrium with the residual melt, thus continuously changing its composition. No 'cumulate' is formed during equilibrium crystallisation.

When a number between 0 and 100 is entered for a phase, this proportion of the phase is continuously 'removed' from contact with the melt preserving its composition, whereas the remainder of the phase re-equilibrates with the continuously evolving melt. See Danyushevsky and Plechov (2011) for further details of the approach.

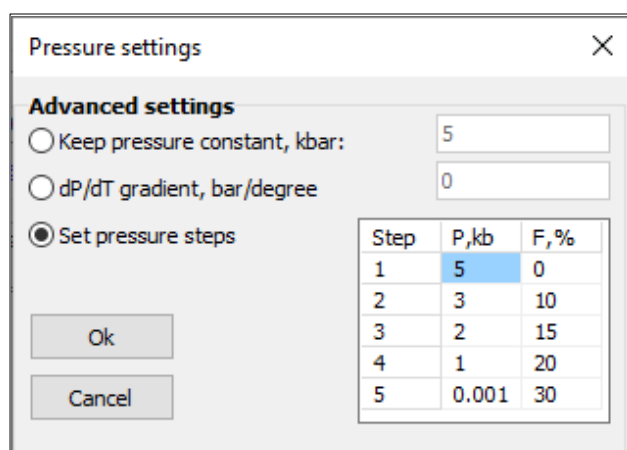


Figure 4.9. The 'Pressure settings' window showing three available options for controlling pressure during calculations.

4.1.3. Setting pressure

Pressure to be used during calculations is set in the 'Pressure' subsection of the Parameters Section (Figs. 1.1, 2.2, 3.1). A value at the onset of calculations (in kbar) can be set in the 'Initial P (kbar)' textbox within this subsection. To set changes to crystallisation pressure during calculations, click on the blue text label below the 'Set Pressure behaviour:' text label in this subsection. This will open the 'Pressure settings' pop-up window (Fig. 4.9).

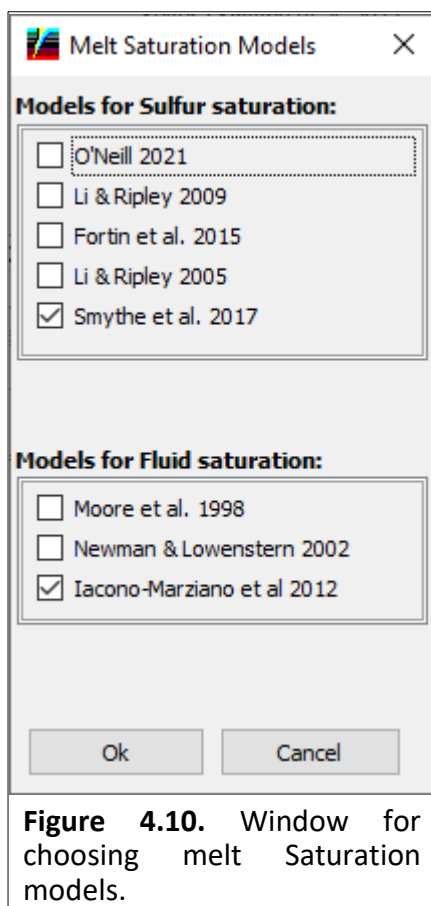
By default, the 'Keep pressure constant' option is chosen.

The 'dP/dT gradient, bar/degree' option allows for pressure to be continuously changed at a fixed rate as a function of temperature. A positive value corresponds to decreasing pressure during crystallisation. If pressure reaches 1 bar before the end of the calculations, it will

remain at 1 bar for the remainder of the calculations. Setting a negative value for the gradient would result in pressure increasing during crystallisation calculations.

The 'Pressure steps' option allows for changing pressure during calculations as a function of the degree of fractionation. Up to four intervals with specific dP/dF values can be set. The dP/dF value for an interval is calculated from the P and F values set as the boundary conditions for this interval. The dP/dF value can equal 0 (pressure is constant) for any number of intervals. To set it to 0, the 'P, kb' value should be the same at the start and end of the fractionation interval. If the F value at the end of the last step is lower than the final F value during calculations, the pressure value at the last step will be used until the end.

The displayed text in the blue text label in the subsection reflects the chosen pressure option: 'Keep constant', ' $dP/dT = \text{'Value'}$ ', or ' dP/dF '.



4.1.4. Setting fluid and sulphur saturation models

Performing calculations in Petrolog4 requires that saturation models for fluid and sulphur in the melt are selected. When software starts, default models are automatically selected. The selected models are displayed in the 'Fluid and Sulphur Saturation Models' subsection of the Parameters section of the Main form (Figs 1.1, 2.2, 3.1). The selected models can be changed by clicking the blue 'Change Saturation Models:' text label in this subsection to open the 'Melt Saturation Models' pop-up window (Fig. 4.10). The available models are listed in Appendix 1.

Click 'Ok' to save the chosen model. Pressing 'Cancel' closes the form without applying any changes.

When the concentrations of volatile elements (H_2O and CO_2) in the melt exceed their solubility values for a given pressure, melt composition and temperature, a separate fluid phase is formed. When the concentration of S^{2-} in the melt exceeds its saturation value, a separate sulphide phase is formed. Similarly to silicate minerals, the fluid and sulphide phases may either remain in the magma or fractionate (see section 4.1.2).

Petrolog4 also offers an option to perform calculation under fluid-saturated and sulphide-saturated conditions. To use these options, check the 'Fluid saturated' and 'Sulphide saturated' checkboxes within the 'Starting melt composition' subsection of the Parameters section of the main form (Figs. 1.1, 2.2, 3.1).

Note: When H_2O and/or CO_2 are present in the starting composition, the user must select a fluid-melt equilibrium model to enable calculations, even if it is not expected that fluid saturation will be reached.

Note: When S^{2-} is present in the starting composition, the user must select a sulphide-melt equilibrium model to enable calculations, even if it is not expected that sulphide saturation will be reached.

Note: When the starting melt composition is significantly fluid-oversaturated at the pressure chosen for calculation (i.e., the concentrations of volatiles in the starting composition are significantly higher than the saturation values), its volatile contents (H_2O and CO_2) will be adjusted to reflect fluid saturation at the chosen pressure.

Note: When the 'VolatileCalc' model for the fluid composition is chosen, the fluid saturation model of Newman and Lowenstern (2002) must be selected (and vice versa). If calculation pressure is set to < 100 bars, it will be changed to 100 bars as this is the minimum calculation pressure required by the model. If the melt CO_2 content decreases below 10 ppm, calculations will be stopped as this model was not meant to be used with such compositions.

Note: When the 'Pure H_2O ' model for fluid composition is selected, the fluid saturation model of Moore et al. (1998) must be selected (and vice versa).

Note: When the ‘Iacono-Marziano et al 2012’ model for fluid composition is selected, the fluid saturation model of Iacono-Marziano et al. (2012) must be selected (and vice versa).

4.1.5. Setting melt oxidation state

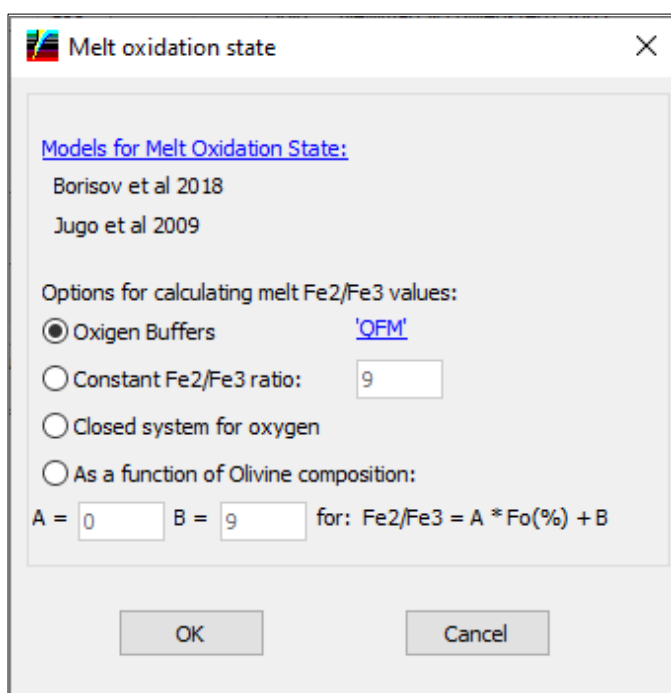


Figure 4.11. Window for choosing options for setting melt oxidation state.

The melt oxidation state (i.e., the proportions of Fe^{2+} / Fe^{3+} and S^{2-} / S^{6+} in the melt) during calculations is set in the ‘Oxidation state’ subsection of the Parameters Section (Figs. 1.1, 2.2, 3.1).

The currently chosen method for controlling melt oxidation state is displayed in the blue text label below ‘Calculations performed using:’ text label. When Petrolog4 starts, the quartz-magnetite-fayalite (QFM) oxygen buffer is selected by default. To change the selected method, click on the blue text label with the currently selected method, to open the ‘Melt oxidation state’ pop-up window (Fig. 4.11).

Four options for controlling melt oxidation state are available: 1) calculation along an oxygen buffer; 2) calculation with a constant $\text{Fe}^{2+}/\text{Fe}^{3+}$ value; 3) calculation assuming a closed system for oxygen, and 4) defining melt oxidation state as a function of liquidus olivine composition (Fig. 4.11).

When calculations are performed assuming a closed system for oxygen, the melt oxidation state is controlled by 1) removal of ferrous and ferric Fe by crystallising silicate and oxide minerals; 2) removal of ferrous Fe and S^{2-} by separation of an immiscible sulphide in sulphide-saturated magmas; and 3) by degassing of sulphur species in fluid-saturated magmas. Petrolog4 maintains equilibrium between oxidation states of Fe and S.

Note: Sulphur oxidation state in the starting composition is calculated from the melt oxidation state as defined either by the oxygen fugacity or the oxidation state of Fe, regardless of S speciation defined in the starting composition (i.e., regardless of whether sulphur content is entered as S or SO_3).

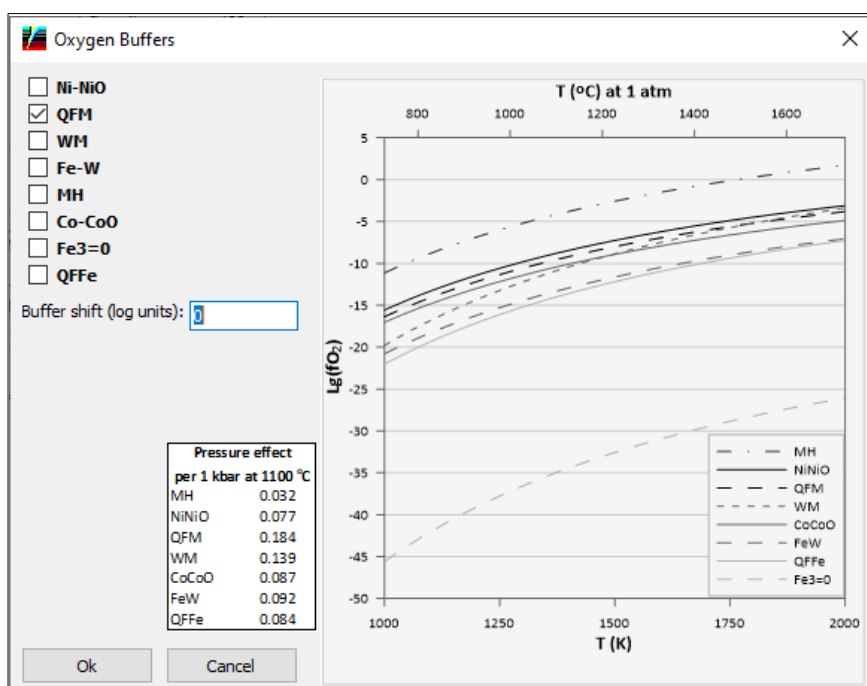


Figure 4.12. Window for choosing buffers of oxygen fugacity for controlling melt oxidation state during calculations.

Note: Choosing the ‘Closed system for oxygen’ option requires that ferric and ferrous Fe contents are defined in the starting composition. If the ferrous Fe content in the starting composition is 0, the calculations will be performed following the Magnetite-Hematite buffer of oxygen fugacity. If the ferric Fe content is set to 0, the calculations will be performed assuming that all Fe and all S in the starting composition are in the reduced form and no oxidised species will be present during fractionation.

When calculations are performed along an oxygen buffer, to change the selected buffer click on the blue text

label next to the 'Oxygen Buffers' bullet point that shows the currently selected buffer (Fig. 4.11). This opens the 'Oxygen Buffers' pop-up window (Fig. 4.12). This window contains a plot comparing oxygen fugacity values along various buffers.

To choose a buffer click on one of the check boxes next to the buffer name. You can also specify a shift from the buffer in log10 units of fO_2 by specifying a positive or negative value in the 'Buffer shift (log units):' text box. The equations for each of the buffers is listed in Appendix 1.

Close this window by pressing the 'Ok' button. Pressing the 'Cancel' button closes the window without applying the changes made.

Performing calculations in Petrolog4 requires that models for Fe and S oxidation states in the silicate melt are selected. When software starts, default models are automatically selected. The selected models are displayed in the bottom part of the 'Oxidation state' subsection of the Parameters section of the Main form (Figs 1.1, 2.2, 3.1). The selected models can be changed by clicking the blue 'Change Oxidation Models:' text label in this subsection to open the 'Melt Oxidation State Models' pop-up window (Fig. 4.13). The available models are listed in Appendix 1. This form can also be opened from the 'Melt Oxidation State' window (Fig. 4.11).

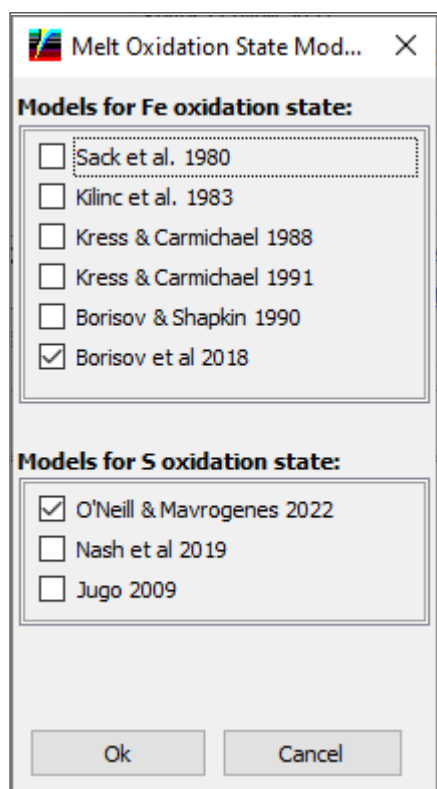


Figure 4.13. Window for choosing models setting melt Fe and S oxidation states.

When using an oxygen buffer to define melt oxidation state, the Fe^{2+} / Fe^{3+} and S^{2-} / S^{6+} values in the melt will be calculated from the oxygen fugacity value corresponding to the chosen buffer, following the chosen models for the oxidation state.

When using a constant Fe^{2+} / Fe^{3+} value to set melt oxidation state, oxygen fugacity and S^{2-} / S^{6+} are calculated from the Fe^{2+} / Fe^{3+} value of the melt following the chosen model for Fe oxidation state (Fig. 4.13).

If the melt oxidation state is defined as a function of liquidus olivine composition (Fig. 4.11), specify values for coefficients A and B for the equation $(Fe^{2+}/Fe^{3+})_{melt} = A \cdot Fo + B$, where Fo is the proportion of forsterite in the liquidus olivine in mol%. For a detailed description of this technique, see Danyushevsky and Sobolev, 1996. When using this option to set melt oxidation state, oxygen fugacity and S^{2-} / S^{6+} are calculated from the Fe^{2+} / Fe^{3+} value of the melt following the chosen model for Fe oxidation state (Fig. 4.13).

Note: This option is only available when olivine has been chosen for calculations in the 'Models for phase-melt equilibrium' subsection window.

4.1.6. Choosing models to calculate melt physical properties

Petrolog4 calculates melt density and viscosity during melt evolution. To choose from the available models, click on the blue text labels within the 'Melt physical properties' subsection of the Parameters Section (Figs. 1, 2.2, 3.1). Clicking on the blue text label next to 'Density:' opens the 'Density Models' pop-up window (Fig.

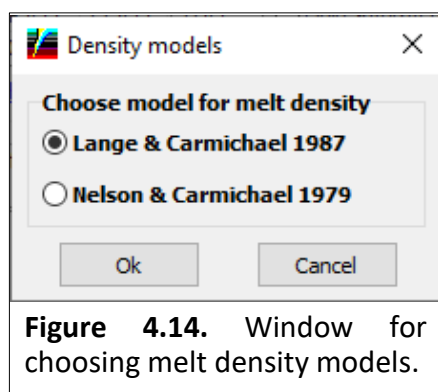


Figure 4.14. Window for choosing melt density models.

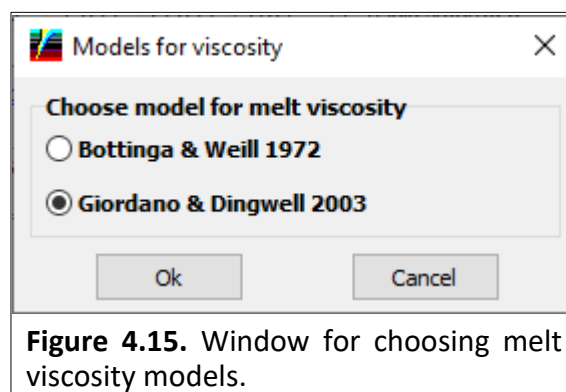


Figure 4.15. Window for choosing melt viscosity models.

4.14). Chose the desired model by pressing on one of the radio buttons next to model names. The available models are listed in Appendix 1. Close the window by pressing the 'Ok' button. Pressing the 'Cancel' button closes the window without applying the changes made.

Clicking on the blue text label next to 'Viscosity:' opens the 'Models for Viscosity' pop-up window (Fig. 4.15). Choose the desired model by pressing on one of the radio buttons next to model names. The available models are listed in Appendix 1. Close the window by pressing the 'Ok' button. Pressing the 'Cancel' button closes the window without applying the changes made.

4.1.7. Setting calculation step

A value for the calculation step is set in the 'Calculation step' text box inside the 'Calculation Parameters' sub-section in the Parameters Section (Figs. 1.1, 2.2, 3.1). The calculation step determines the amount (in wt%) by which the melt mass decreases at each step of crystallisation calculations. The smaller the calculation step is the more precise the calculations are, but this also leads to the same calculations taking longer. The default value of 0.01% of the amount of melt on each step provides acceptable precision and reasonably short calculation times. For implications of using larger and smaller crystallisation steps see Danyushevsky and Plechov, 2011. It is not recommended to increase the calculation step.

Note: The algorithm used in Petrolog4 is designed with an assumption that the output of the intermediate states of the system during calculations would occur at frequencies which are at least 2 orders of magnitude larger than the calculation step. For example, if the calculation step is set to 0.01%, the smallest recommended output frequency is 1%.

4.1.8. Setting conditions for the frequency of results output during calculations

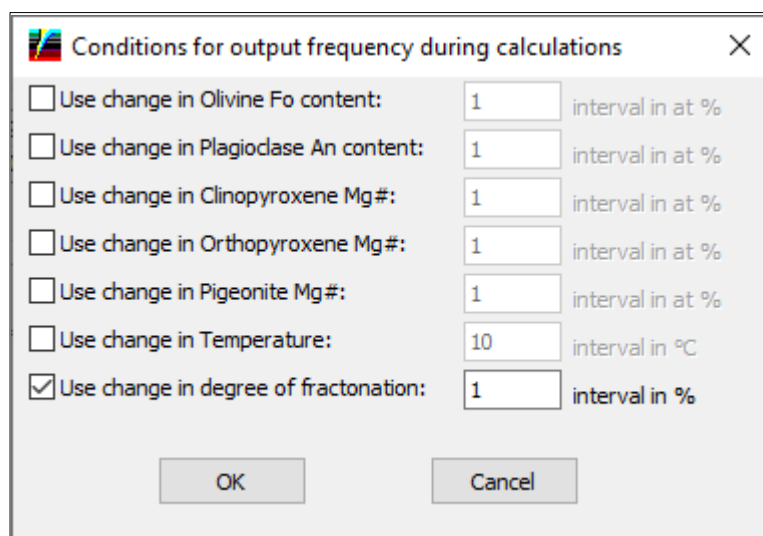


Figure 4.16. The 'Conditions for output frequency during calculations' window showing options available for setting conditions for the output of the intermediate states of the system during calculations.

Petrolog4 offers several options for setting output frequency of the intermediate states of the system during calculations. The default setting is 1 wt% of crystallisation. To change this setting, click on the blue text label below 'Define output frequency:' text label inside the 'Calculation Parameters' sub-section in the Parameters Section (Figs. 1.1, 2.2, 3.1). This will open the 'Conditions for output frequency during calculations' pop-up window (Fig. 4.16). Several options can be set simultaneously, and the program will display the intermediate states of the system satisfying all the selected criteria.

Close the window by pressing the 'Ok' button. Pressing the 'Cancel' button closes the window without applying the changes made. The blue label will display the chosen option(s).

An example of the output of an intermediate state of the system during calculations is shown in Tables 1 and 2.

The first line of the output is the magma composition at the given stage of evolution. The second line is the composition of the melt. If only some proportions of some of the phases fractionate from the magma (as is the case for the example in Tables 1, 2), the composition of the magma is different from the composition of the melt.

Below the melt are the compositions of all phases that are currently crystallising from the melt. These follow by a line with phase compositional parameters of the crystallising phases (mol% forsterite (Fo) for Olivine; mol% anorthite (An) for Plagioclase; Mg# ($100 \cdot \text{Mg}/(\text{Mg} + \text{Fe})$) for Clinopyroxene; Orthopyroxene; Pigeonite;

Ilmenite and Magnetite; Cr# ($100 \cdot \text{Cr} / (\text{Cr} + \text{Al})$) for Spinel; Fe# ($100 \cdot \text{Fe} / (\text{Ni} + \text{Fe})$) for sulphide; and CO2# ($100 \cdot \text{CO}_2 / (\text{CO}_2 + \text{H}_2\text{O})$ in mol units) for fluid).

The next line displays melt temperature, oxygen fugacity, and pseudo-liquidus temperature for those minerals that are not on the liquidus of the current melt. In the first example in Table 2, orthopyroxene and sulphide are the only phases on the liquidus of the melt at 2% of crystallisation, whereas in the second example orthopyroxene, plagioclase, sulphide and fluid are on the liquidus of the melt at 15% of crystallisation.

The next line contains weight proportions of all phases in the magma.

The next line shows crystallisation pressure, melt density and viscosity.

When some proportions of some of the phases fractionate from the magma (as is the case for the example in Tables 1, 2), the composition of fractionated phases is shown under the line with crystallisation pressure. The first line shows the composition of the combined fractionated phases called 'Cumulate'.

The next lines show bulk compositions of all fractionated phases at the given extent of melt evolution. The bulk compositions for each phase are calculated by mass-balancing fractionated compositions continuously formed during crystallisation.

The next line shows bulk fractionated phase compositional parameters. In most cases these will be higher (more primitive) than the composition currently crystallising from the melt (see Danyushevsky and Plechov, 2011 for more details).

The last line contains weight proportions of all phases in the magma.

4.1.9. Setting conditions to stop calculations

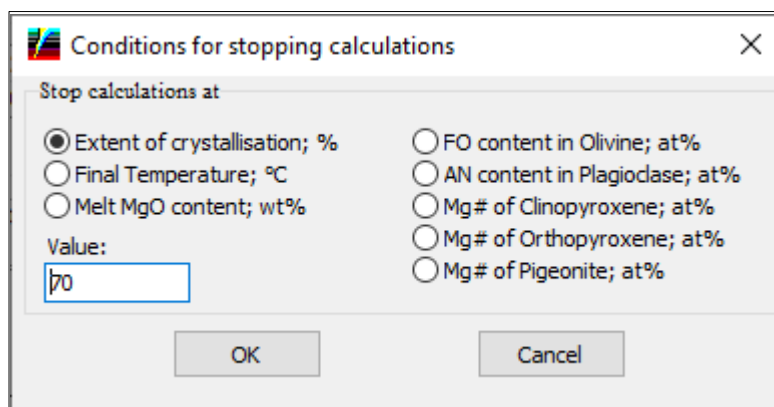


Figure 4.17. The 'Conditions for stopping calculation' window showing options available for setting conditions for stopping calculations.

Petrolog4 offers several options for defining conditions for stopping calculations. The default setting is 0 wt% of crystallisation, indicating that no crystallisation calculation is performed. To change this setting, click on the blue text label below 'Define conditions to stop calculations:' text label inside the 'Calculation Parameters' sub-section in the Parameters Section (Figs. 1.1, 2.2, 3.1). The 'Conditions for stopping calculations' window will pop-up (Fig. 23). The user must choose one of the available options.

Close the window by pressing the 'OK' button. Pressing the 'Cancel' button closes the window without applying the changes made. The blue label will display the chosen option.

Note: The data file can contain columns that contain conditions to stop calculations that can differ for each analysis. Such columns should have the following name in the header row: LASTFRAC, LASTTEMP, LASTMGO, LASTFO, LASTAN, LASTCPX, LASTOPX, LASTPIG corresponding to the options shown on Fig. 4.17. The parameters should be in the same units as shown on Fig. 4.17.

Table 1. Example output: Calculation parameters and the starting composition

Modelling Crystallisation

Phases chosen for calculations are:

Olv, Plg, Cpx, Opx, Pig, Slf, Fld

The model used for Olv is: Herzberg & O'Hara 2002

Olv fractionation is: 80.00 %

The model used for Plg is: Ariskin et al. 1993

Plg fractionation is: 50.00 %

The model used for Cpx is: Ariskin et al. 1993

Cpx fractionation is: 70.00 %

The model used for Opx is: Bolikhovskaya et al. 1996

Opx fractionation is: 70.00 %

The model used for Pig is: Bolikhovskaya et al. 1996

Pig fractionation is: 70.00 %

The model used for Slf is: Fe Sulfide

Slf fractionation is: 100.00 %

The model used for Fld is: VolatileCalc 2002

Fld fractionation is: 100.00 %

Fe2O3 in the melt is calculated using QFM buffer of oxygen fugacity

following the model of Borisov et al 2018

SO3 in the melt is calculated using the model of Jugo et al 2009

Fluid saturation of the melt is calculated using the model of Newman & Lowenstern 2002

Sulfur saturation of the melt is calculated using the model of Li & Ripley 2009

Initial Pressure = 5 kbar

During calculations Pressure is changed at 10 % crystallisation to 3 kbars

at 15 % crystallisation to 2 kbars

at 20 % crystallisation to 1 kbars

at 30 % crystallisation to 0.001 kbars

Ds for minerals:

Mineral	H2O	CO2	S	SO3	Cl	Co	Ni	Rb	Sr	Ba
Olv	0	0	0	0	0	Beatt91	Herzb02	0.001	0.01	0
Plg	0	0	0	0	0	0	0	0.1	Bl_Wo91	Bl_Wo91
Cpx	0	0	0	0	0.001	0.2	1	0.05	0.07	0.03
Opx	0	0	0	0	0.001	0.8	1.5	0.02	0.05	0.015
Pig	0	0	0	0	0.01	0.8	1.2	0.03	0.05	0.02
Slf	0.1	0	FeS	0	0	0	10	0	0	0
Fld	VltlCalc	VltlCalc	0	0.2	0.05	0	0	0.2	0.2	0.3

Melt density is calculated following the model of Lange & Carmichael 1987

Melt viscosity is calculated following the model of Giordano & Dingwell 2003

Parameters to stop calculations at:

Final degree of fractionation: 70 %

The amount of a mineral phase which will be extracted from

100% of melt on each step is: 0.01 %

The starting composition "Analysis1" has been adjusted for the chosen oxidation state, checked for fluid and sulfide saturation, and recalculated to 100 wt%

Since "Sulfide saturated" option is selected, S content in the starting composition has been adjusted to match sulfide saturation.

	SiO2	TiO2	Al2O3	Fe2O3	FeO	MnO	MgO	CaO	Na2O	K2O	P2O5	Cr2O3	H2O_wt%	CO2_ppm	S_ppm	SO3_ppm	Cl_ppm	Co_ppm	Ni_ppm	Rb_ppm	Sr_ppm	Ba_ppm
Start	48.00	1.00	14.00	0.50	9.00	0.16	7.00	9.00	2.00	0.20	0.22	0.08	3.00	1600.0	2000.0	0.0	68.0	60.0	92.0	10.0	226.0	61.0
Melt	50.74	1.06	14.80	1.58	8.57	0.17	7.40	9.51	2.11	0.21	0.23	0.08	3.17	1691.4	1054.5	146.3	71.9	63.4	97.3	10.6	238.9	64.5

Table 2. Example output: intermediate states of the system during calculations at 2% (top) and 18% (bottom) of fractionation of the starting composition shown in Table 1, using a set of calculation parameters shown in Table 1.

	SiO2	TiO2	Al2O3	Fe2O3	FeO	MnO	MgO	CaO	Na2O	K2O	P2O5	Cr2O3	H2O_wt%	CO2_ppm	S_ppm	SO3_ppm	Cl_ppm	Co_ppm	Ni_ppm	Rb_ppm	Sr_ppm	Ba_ppm
Magma	50.72	1.07	14.93	1.55	8.59	0.17	7.09	9.63	2.14	0.21	0.24	0.09	3.22	1715.7	1019.2	141.5	72.9	63.6	96.5	10.7	242.2	65.4
Melt	50.70	1.08	14.98	1.56	8.58	0.17	6.96	9.68	2.16	0.22	0.24	0.09	3.24	1726.1	1025.4	142.3	73.4	63.7	96.2	10.8	243.6	65.8
Opx	53.30		6.05		10.08		28.96	1.59									0.1	51.0	144.3	0.2	12.2	1.0
Slf					63.17								0.32		364133.6				960.3			
Mg#Opx= 83.667; Fe#Slf= 99.856; T=1207.9 (Opx); Lg(fO2)=-7.9 dNNO=-0.5; T0lv=1204.6 TPlg=1204.5 TCpx=1186.6 TPig=1185.8 Amounts (wt%) of phases in magma: Melt 97.9957; Opx 0.5970; Pressure: 4.601 kbar; Density: 2.666 g/cm3; Viscosity: v=35 poise; ln(v)=3.6																						
	SiO2	TiO2	Al2O3	Fe2O3	FeO	MnO	MgO	CaO	Na2O	K2O	P2O5	Cr2O3	H2O_wt%	CO2_ppm	S_ppm	SO3_ppm	Cl_ppm	Co_ppm	Ni_ppm	Rb_ppm	Sr_ppm	Ba_ppm
Cumulate	52.76	0.00	6.10	0.00	10.39	0.00	28.84	1.51	0.00	0.00	0.00	0.00	0.00	0.0	3721.4	0.0	0.1	50.3	153.5	0.2	11.9	1.0
Opx	53.30		6.16		9.84		29.14	1.52									0.1	50.9	145.1	0.2	12.1	1.0
Slf					63.17								0.32		364137.2				965.7			
Mg#Opx= 84.067; Fe#Slf= 99.855; Amounts (wt%) of cumulate phases: Opx 1.3929; Slf 0.0144;																						

	SiO2	TiO2	Al2O3	Fe2O3	FeO	MnO	MgO	CaO	Na2O	K2O	P2O5	Cr2O3	H2O_wt%	CO2_ppm	S_ppm	SO3_ppm	Cl_ppm	Co_ppm	Ni_ppm	Rb_ppm	Sr_ppm	Ba_ppm
Magma	50.81	1.18	14.51	1.46	9.17	0.19	6.50	9.76	2.20	0.24	0.26	0.09	3.44	28.6	955.1	132.6	80.6	67.8	99.1	11.8	242.6	71.2
Melt	50.73	1.29	13.81	1.59	9.62	0.21	6.26	9.72	2.19	0.26	0.28	0.10	3.75	31.2	1039.5	144.3	87.7	72.1	103.4	12.7	236.1	76.3
Opx	54.17		3.60		12.35		28.27	1.57									0.1	57.7	155.1	0.3	11.8	1.1
Plg	50.55		31.65					14.32	3.41											1.3	465.2	19.4
Slf					63.12								0.37		364056.3				1032.4			
Fld													88.70	112878.9		28.9	4.4			2.5	47.2	22.9
Mg#Opx= 80.317; An= 69.857; Fe#Slf= 99.845; CO2#Fl= 4.947; T=1171.8 (Opx); Lg(fO2)=-8.5 dNNO=-0.7; TPlg=1171.8 T0lv=1170.0 TCpx=1159.3 TPig=1156.2 Amounts (wt%) of phases in magma: Melt 81.9986; Plg 4.8697; Opx 2.3810; Pressure: 1.402 kbar; Density: 2.683 g/cm3; Viscosity: v=41 poise; ln(v)=3.7																						
	SiO2	TiO2	Al2O3	Fe2O3	FeO	MnO	MgO	CaO	Na2O	K2O	P2O5	Cr2O3	H2O_wt%	CO2_ppm	S_ppm	SO3_ppm	Cl_ppm	Co_ppm	Ni_ppm	Rb_ppm	Sr_ppm	Ba_ppm
Cumulate	50.31	0.00	17.23	0.00	5.93	0.00	14.87	7.53	1.41	0.00	0.00	0.00	0.93	15498.6	1986.5	0.7	0.1	27.5	81.8	0.7	209.1	8.7
Plg	49.91		32.09					14.83	3.12											1.2	445.3	16.9
Opx	53.61		5.21		10.81		28.77	1.57									0.1	53.2	148.0	0.2	12.1	1.0
Slf					63.15								0.34		364105.5				985.1			
Fld													37.48	625060.6		28.6	4.1			2.4	48.0	21.6
An= 72.456; Mg#Opx= 82.583; Fe#Slf= 99.852; CO2#Fl= 40.549; Amounts (wt%) of cumulate phases: Plg 4.8697; Opx 5.5558; Slf 0.0587; Fld 0.26657;																						

Note: When sulphide composition is displayed, the concentration of iron (not iron oxide) in wt% is shown in the FeO column, i.e., oxygen is not added to iron. When fluid composition is displayed, SO2_ppm is shown in the SO3_ppm column, i.e., the oxidation state of S in the fluid is +4.

Note: The reference oxygen buffer to be used to display relative oxygen fugacity can be set in the Options form (Fig. 2.4). In the example shown above, Ni-NiO has been chosen as the reference buffer (dNNO is displayed).

4.2. Saving and loading calculation parameters

To save the current set of calculation parameters, use the 'Save Parameters' option in the 'File' section of the Main Menu on the main form (Fig. 2.2). In the dialog form that appears, enter a file name and press Save.

Note: Petrolog4 assigns .PtlParam extension to files with parameter values.

Petrolog4 offers options to include the names of either the data file or the file with the saved D values, or both, with the saved parameters. To set these two options, use the 'Petrolog Options' form that is opened by choosing the 'Options' item in the 'Tools' section of the Main Menu (Fig. 2.4)

To load a previously saved set of calculation parameters, use the 'Load Parameters' option in the 'File' section of the Main Menu on the main form (Fig. 2.2). Chose the file in the dialog window, and press Open.

4.2.1. Saving the Default Set of calculation parameters.

To save the current set of calculation parameters as the Default Set, use the 'Save Parameters as the Default Set' option in the 'File' section of the Main Menu on the main form (Fig. 2.2). Once saved, this set of parameters will be loaded every time Petrolog4 starts. To reload this set of parameters while using Petrolog4, use 'Load the Default Set of Parameters' option in the 'File' section of the Main Menu on the main form (Fig. 2.2).

Note: The Program Default set of parameters can be restored by using the 'Reset Program Defaults' option of the Tools Menu (Fig. 3.1).

4.3. Structure of output files

During modelling of crystallisation, Petrolog4 saves the following files:

FileName_FRAC_calc_param.csv file lists values of all calculation parameters.

FileName_FRAC.csv file contains magma, melt and cumulate composition, proportions of all phases in the magma and cumulate, compositional parameters of phases crystallising from the magma and bulk phase in the cumulate, temperature, pressure and melt physical properties.

Note: When exporting results of previous calculations to Excel, the user must click on the FileName_FRAC.csv file to initiate export.

Compositions of each phase in equilibrium with the melt at each recorded stage of fractionation are saved in a separate file. Such files have the following names:

FileName_FRAC_calc_Olv.csv for olivine compositions;

FileName_FRAC_calc_Plg.csv for plagioclase compositions;

FileName_FRAC_calc_Cpx.csv for clinopyroxene compositions;

FileName_FRAC_calc_Opx.csv for orthopyroxene compositions;

FileName_FRAC_calc_Pig.csv for pigeonite compositions;

FileName_FRAC_calc_Spl.csv for spinel compositions;

FileName_FRAC_calc_Ilmen.csv for ilmenite compositions;

FileName_FRAC_calc_Mgt.csv for magnetite compositions;

FileName_FRAC_calc_Slf.csv for sulphide compositions;

FileName_FRAC_calc_Fld.csv for fluid compositions.

Note: File that are saved during each calculation are only for those phases that have appeared on the liquidus during calculations.

5. Melt Liquidus association

To determine melt liquidus association, choose 'Melt liquidus association' tab of the Main form (Fig. 5.1).

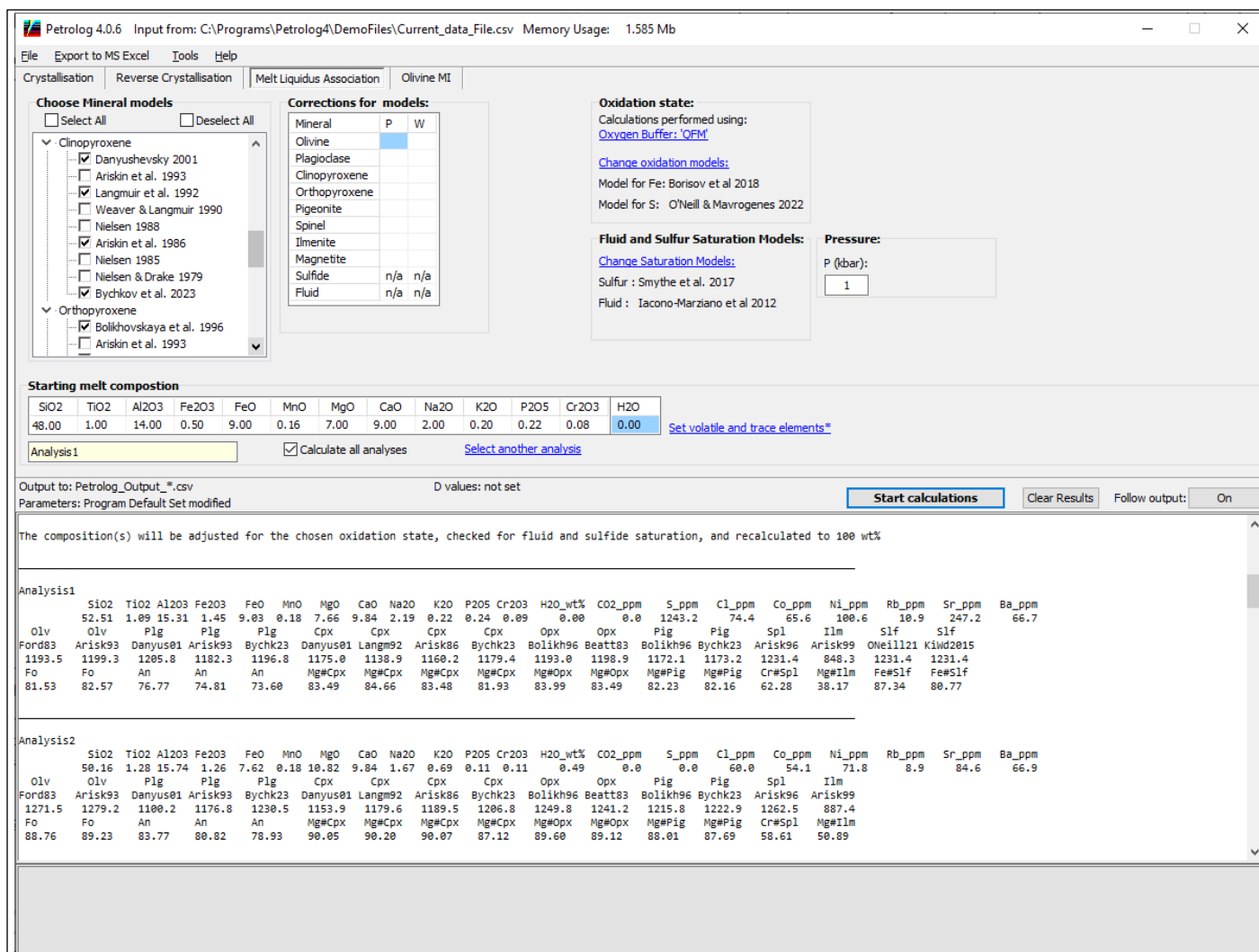


Figure 5.1. ‘Melt Liquidus Association’ option of Petrolog4 interface.

Note: It is recommended that you read Section 4 of this manual before reading this section.

In this option, Petrolog4 does not model a crystallisation path but calculates pseudo-liquidus temperatures and liquidus phase compositions for a chosen set of phases and phase-melt equilibrium models. The following phase compositional parameters are also calculated:

Olivine:	mol% forsterite (Fo);
Plagioclase:	mol% anorthite (An);
Clinopyroxene; Orthopyroxene; Pigeonite; Ilmenite and Magnetite:	Mg# ($100 * \text{Mg} / (\text{Mg} + \text{Fe})$);
Spinel:	Cr# ($100 * \text{Cr} / (\text{Cr} + \text{Al})$);
Sulphide:	Fe# ($100 * \text{Fe} / (\text{Fe} + \text{Ni})$);
Fluid (mol units):	CO2# ($100 * \text{CO}_2 / (\text{CO}_2 + \text{H}_2\text{O})$).

By comparing calculated temperatures for different phases, the liquidus association of a melt composition can be established. As the stated errors for most models are $\sim 15 - 20^\circ\text{C}$, the liquidus association should include the phase(s) with the highest calculated temperature (i.e., the liquidus temperature) and phases which pseudo-liquidus temperatures are within $\sim 20^\circ\text{C}$ of the calculated liquidus temperature.

Note: During melt liquidus association calculations it is possible to choose any number of models for each phase. This allows a comparison to be made between different models.

Note: If the starting composition is sulphide or fluid saturated, the established liquidus temperature is assigned to these phases and used for calculating their compositions.

Note: The oxidation states of Fe and S in the melt composition recorded in the results output correspond to the established liquidus temperature (i.e., the highest calculated temperature among the models chosen for calculation).

When models of Danyushevsky (2001) for olivine AND plagioclase are chosen, Petrolog4 automatically estimates the H₂O content in the melt which is required for the starting composition to lie on an olivine + plagioclase cotectic.

If models of Danyushevsky (2001) for olivine AND clinopyroxene are chosen, Petrolog4 automatically estimates crystallisation pressure at which the starting composition has both olivine and clinopyroxene on its liquidus.

Note: Models of Danyushevsky (2001) are calibrated for MORB and BABB compositions only and should not be used for calculations with compositions from other tectonic settings.

Since crystallisation calculations are not performed under this Option, the number of calculation parameters that can be set by the user is limited.

Corrections to the calculated liquidus temperatures for the effects of pressure and melt H₂O contents are set in the 'Correction for models:' subsection of the Parameters Section of the Main form (Fig. 5.1) in the same way as for Crystallisation calculations (see sections 4.1.1.1 and 4.1.1.2).

Note: The same correction will apply to all models selected for a phase.

Fluid and sulphur saturation models are set in the 'Fluid and Sulphur Saturation models:' subsection of the Parameters Section of the Main form (Fig. 5.1) in the same way as for Crystallisation calculations (see section 4.1.4).

Melt oxidation state is set in the 'Oxidation state' subsection of the Parameters Section of the Main form (Fig. 5.1) in the same way as for Crystallisation calculations (see section 4.1.5).

Pressure is set in the 'Pressure' subsection of the Parameters Section of the Main form (Fig. 5.1).

5.1. Saving and loading calculation parameters and structure of output files

Saving and Loading calculation parameters is done in the same way as for Crystallisation calculations (see section 4.2).

During melt liquidus association calculations, Petrolog4 saves the following files:

FileName_MLA_calc_param.csv file lists values of all calculation parameters.

FileName_MLA.csv file contains the starting melt composition, and pseudo-liquidus temperatures and compositional parameters of phases for the selected models.

Note: When exporting results of previous calculations to Excel, the user must click on the FileName_MLA.csv file to initiate export.

Compositions of each phase in equilibrium with the melt are saved in a separate file that have the same naming convention as for Crystallisation calculations (e.g., file FileName_MLA_Olv.csv contains olivine compositions).

6. Reverse of fractional crystallisation

To model reverse of fractional crystallisation, choose 'Reverse Crystallisation' tab of the Main form (Fig. 6.1).

Petrolog 4.0.4 Input from: C:\Programs\PETROLOG\Current_data_File.csv

File Export to MS Excel Tools Help

Crystallisation Reverse Crystallisation Melt Liquidus Association Olivine MI

Mineral-melt models:

Phase	Model	P	W	Tr
Olivine	Herzberg & O'Hara 2002	Y		Y
Plagioclase	Ariskin et al. 1993	Y		
Clinopyroxene	Ariskin et al. 1993	Y		
Orthopyroxene	Bolikhovskaya et al. 1996	Y		
Pigeonite	Bolikhovskaya et al. 1996	Y		
Spinel	Press to Select			
Ilmenite	Press to Select			
Magnetite	Press to Select			
Sulfide	Fe Sulfide			Y
Fluid	VolatileCalc 2002	Y		Y

☐ Force Pl-OI cotectic

Parameters for exsolution:

Plagioclase [press to set](#)
 Orthopyroxene [press to set](#)
 Clinopyroxene [press to set](#)
 Pigeonite [press to set](#)
 Magnetite [press to set](#)
 Ilmenite [press to set](#)
 Sulfide [press to set](#)
 Fluid [press to set](#)

Oxidation state:
 Calculations performed using:
[Oxygen Buffer: 'QFM'](#)
[Change Oxidation Models:](#)
 Model for Fe: Borisov et al 2018
 Model for S: Jugo 2009

Melt physical properties:
 Density: [Lange & Carmichael 1987](#)
 Viscosity: [Giordano & Dingwell 2003](#)

Calculation parameters:
 Calculation step: %
 Define output frequency:
[Fractionation step = 1.0 %](#)
 A total of 1 output condition(s) chosen
 Define conditions to stop calculations:
[Extent of fractionation = 70 %](#)

Fluid and Sulfur Saturation Models:
[Change Saturation Models:](#)
 Sulfur : Li & Ripley 2009
 Fluid : Newman & Lowenstern 2002

Pressure:
 Initial P (kbar):
 Set Pressure behaviour:
[dP/dF](#)

Starting melt composition:

SiO2	TiO2	Al2O3	Fe2O3	FeO	MnO	MgO	CaO	Na2O	K2O	P2O5	Cr2O3	H2O
48.00	1.00	14.00	0.50	9.00	0.16	7.00	9.00	2.00	0.20	0.22	0.08	3.00

☐ Fluid saturated ☒ Sulfide saturated
[Set volatile and trace elements*](#)

Analysis1 ☐ Calculate all analyses [Select another analysis](#)

Output to: Petrolog_Output_*.csv D values: loaded from Current_D_set.PtParamSet

Parameters: last loaded from Current_Param.PtParam modified

Start calculations **Clear Results** Follow output: ☒ On

Modelling reverse of fractional crystallisation
 Phases chosen for calculations are:
 Oliv, Plg, Cpx, Opx, Pig, Slf, Fld
 The model used for Oliv is: Herzberg & O'Hara 2002
 The model used for Plg is: Ariskin et al. 1993
 The model used for Cpx is: Ariskin et al. 1993
 The model used for Opx is: Bolikhovskaya et al. 1996
 The model used for Pig is: Bolikhovskaya et al. 1996
 The model used for Slf is: Fe Sulfide
 The model used for Fld is: VolatileCalc 2002
 Fe2O3 in the melt is calculated using QFM buffer of oxygen fugacity following the model of Borisov et al 2018
 SO3 in the melt is calculated using the model of Jugo 2009
 Fluid saturation of the melt is calculated using the model of Newman & Lowenstern 2002
 Sulfur saturation of the melt is calculated using the model of Li & Ripley 2009
 Initial Pressure = 2 kbar
 during calculations Pressure is increased at 10 % crystals added to 3 kbars
 at 15 % crystals added to 2 kbars
 at 20 % crystals added to 1 kbars
 at 30 % crystals added to 0.001 kbars

Ds for minerals:

Mineral	H2O	CO2	S	SO3	Cl	Co	Ni	Rb	Sr	Ba
Olv	0	0	0	0	0	Beatt91	Herzb02	0.001	0.01	0
Plg	0	0	0	0	0	0	0	0.1	B1_M091	B1_M091
Cpx	0	0	0	0	0.001	0.2	1	0.05	0.07	0.03

Figure 6.1. 'Reverse crystallisation' option of Petrolog4 interface.

Note: It is recommended that you read Sections 4 and 5 of this manual before reading this section.

The algorithm of modelling the reverse of fractional crystallisation involves addition of phases that crystallized from the melt back to the melt composition thus moving it up along a cotectic (a liquid line of descent) towards more primitive compositions.

Unlike crystallisation calculations, where crystallisation of any number of phases can be modelled for any starting composition (as the algorithm determines which minerals actually crystallize from the melt), the phases that are included in the reverse of fractionation calculations must be on the liquidus of the starting composition at the chosen calculation parameters.

Note: Phases that are present on the liquidus of the starting composition can be checked using the 'Melt liquidus association' option (see section 3 of this manual).

Unlike crystallisation calculations, where the mineral with the highest pseudo-liquidus temperature is subtracted from the melt composition, the mineral with the lowest pseudo-liquidus temperature is added to the melt composition during reverse of fractionation calculations. The technique is least ambiguous when used with compositions that lie within a single-phase saturation field.

Note: It is possible to calculate the reverse of pure fractional crystallisation only, as equilibrium crystallisation does not preserve sufficient information on the crystallisation history to enable reverse calculations.

Unlike crystallisation calculations, the algorithm for modelling the reverse of fractionation does not have a built-in mechanism for determining when minerals appeared on the liquidus during fractionation, and thus these conditions should be set by the user. Consider an example with a melt composition having the following crystallisation sequence: first olivine, then plagioclase after 5% crystallisation (crystallisation along an olivine+plagioclase cotectic), and then clinopyroxene after 15% crystallisation (crystallisation along an olivine+plagioclase+clinopyroxene cotectic), with a total extent of crystallisation of 25%. Reversing this crystallisation sequence using the evolved melt composition formed after 25% of crystallisation would start with reversing crystallisation along the olivine+plagioclase+clinopyroxene cotectic. However, the algorithm cannot determine when clinopyroxene (or plagioclase) appeared on the liquidus during fractionation, and the timing of these events should be set by the user. Thus, the calculated trend of melt evolution is dependent on the conditions at which minerals are excluded from calculations to force the trend off a cotectic.

The parameters at which the melt moves off a given cotectic (i.e., parameters for phase exclusion) are set in the 'Parameters for Exclusion' subsection of the Parameters section of the Main form (Fig. 6.1). Click on the blue text label ('press to set') next to the desired mineral to open the 'Conditions for exclusion' pop-up window for this mineral (Fig. 6.2).

Figure 6.2. The 'Conditions for exclusion' window, showing four available options for specifying timing of plagioclase exclusion from calculations.

Petrolog4 offers four different options for setting the timing of exclusion for plagioclase and pyroxenes: 1) temperature; 2) melt MgO content; 3) composition of liquidus olivine; 4) the composition of the phase. For other phases the available options are temperature and melt MgO content. Several options can be set simultaneously, and the mineral will be excluded when any of the set conditions are met.

Close the window by pressing the 'Ok' button. Pressing the 'Cancel' button closes the window without applying the changes made. The blue label on the Main form will display the chosen option(s).

All other parameters for reverse of fractional crystallisation calculations are set in exactly the same way as for crystallisation calculation (see Section 4 of this manual).

Note: The data file can contain columns that contain conditions to stop calculations that can differ for each analysis. See section 4.1.8. for more details).

6.1. Saving and loading calculation parameters and structure of output files

Saving and loading calculation parameters is done in the same way as for Crystallisation calculations (see section 4.2).

During reverse of fractional crystallisation calculations, Petrolog4 saves the following files:

FileName_REV_calc_param.csv file lists values of all calculation parameters.

FileName_REV.csv file contains the starting melt composition, and pseudo-liquidus temperatures and compositional parameters of phases for the selected models.

Note: When exporting results of previous calculations to Excel, the user must click on the FileName_REV.csv file to initiate export.

Compositions of each phase in equilibrium with the melt are saved in a separate file that have the same naming convention as for Crystallisation calculations (e.g., file FileName_REV_Olv.csv contains olivine compositions).

7. Modelling post-entrapment re-equilibration of melt inclusions in olivine

To model post-entrapment re-equilibration of melt inclusions in olivine, chose 'Olivine MI' tab of the Main form (Fig. 7.1).

Petrolog 4.0.4 Input from: C:\Programs\PETROLOG\Current_data_File.csv

File Export to MS Excel Tools Help

Crystallisation Reverse Crystallisation Melt Liquidus Association **Olivine MI**

Type of Calculations:

☒ Reconstruct MI composition

☐ Model diffusion profiles

Olivine model: [Herzberg O'Hara 2002](#) Oxidation state: [Oxygen Buffer: 'QFM'](#)

Density model: [Lange & Carmichael 1987](#) Fe-Mg diff. model: [Chakraborty 1997](#)

Set of minor elements (Ca, Mn, Cr) in Olivine

☒ None ☐ High-Ca boninites

☐ Komatiites ☐ MORB or BABB

Reconstructing MI composition to a given FeO* content in the trapped melt

Starting melt composition

SiO2	TiO2	Al2O3	Fe2O3	FeO	MnO	MgO	CaO	Na2O	K2O	P2O5	Cr2O3	H2O
48.00	1.00	14.00	0.50	9.00	0.16	7.00	9.00	2.00	0.20	0.22	0.08	3.00

Analysis1

☐ Calculate all analyses from the file [Select another analysis](#) [Set volatile and trace elements*](#)

Model diffusion profiles

Inclusion radius, microns: 150

Cooling interval, °C: 100

☐ Simulate reheating experiment:

Output to: Petrolog_Output_*.csv D values: loaded from Current_D_set.PtIDSet

Parameters: last loaded from Current_Param.PtParam modified

Start calculations **Clear Results** Follow output: **On**

Correcting MI in olivine for post-entrapment re-equilibration

The model used for olv is: Herzberg & O'Hara 2002

Fe2O3 in the melt is calculated using QFM buffer of oxygen fugacity following the model of Borisov et al 2018

SO3 in the melt is calculated using the model of Jugo 2009

Calculation Pressure = 1 atm

Choice for minor elements in olivine (Ca Mn Cr) is: all set to 0

***** Warning!!! *****

The chosen olivine model does not incorporate the effect of H2O and no correction for H2O has been set.

DS for Olivine:

Mineral	H2O	CO2	S	SO3	Cl	Co	Ni	Rb	Sr	Ba
Olv	0	0	0	0	0	Beatt91	Herzb02	0.001	0.01	0

T_run	T_calc	MgO	Fo_h	Fo_c	FeO*f	FeO*m	No	Analysis
1193.1	1193.1	7.42	88.00	83.88	7.00	9.72	1	Analysis1
1193.1	1193.1	7.45	88.00	84.29	7.00	9.46	1	Analysis1
1193.1	1193.1	7.48	88.00	84.70	7.00	9.21	1	Analysis1
1193.1	1193.1	7.51	88.00	85.12	7.00	8.95	1	Analysis1
1193.1	1193.1	7.54	88.00	85.53	7.00	8.69	1	Analysis1
1193.1	1193.1	7.57	88.00	85.95	7.00	8.43	1	Analysis1
1193.1	1193.1	7.60	88.00	86.36	7.00	8.17	1	Analysis1
1193.1	1193.1	7.63	88.00	86.78	7.00	7.91	1	Analysis1

12:00:00 AM sec

Figure 7.1. 'Olivine MI' option of Petrolog4 interface for reconstructing melt inclusion compositions.

Note: It is recommended to read Sections 4, 5 and 6 of this manual before reading this section.

7.1. Reconstructing the initial trapped composition of the MI

Re-equilibration of Fe and Mg between melt inclusions and their host olivine phenocrysts is described in detail by Danyushevsky *et al.* (2000a, 2002), with the main points summarised briefly below. The underlying assumption in these considerations is that the composition of the host olivine does not change after trapping of the melt inclusion.

Cooling of an inclusion after trapping results in crystallisation of olivine from the trapped melt, forming an olivine rim on the walls of the inclusion. The crystallising olivine rim is progressively enriched in Fe and depleted in Mg, i.e., becomes poorer in forsterite component, resulting in a compositional gradient within the rim. The existence of this compositional gradient causes re-equilibration of the inclusion with its host. This re-equilibration is achieved by diffusion of Fe out of, and Mg into the initial volume of the inclusion. This leads to a rapid decrease in Fe content of the residual melt inside the inclusion, a process referred to as 'Fe-loss' by Danyushevsky *et al.* (2000a).

Conversely, if an olivine grain containing a melt inclusion is heated over the temperature of inclusion entrapment, host olivine around the inclusion would melt, increasing the Mg# of the melt inside the inclusion and resulting in disequilibrium between the melt and host olivine. This leads to re-equilibration of the melt with the host, which is achieved by diffusion of Fe into, and Mg out of the melt inside the

inclusion. This leads to a rapid increase in Fe content of the melt, a process that can be referred to as 'Fe-gain'.

Petrolog4 offers an option of reconstructing the initially trapped melt composition, providing that the user specifies the FeO* content of the trapped melt. The algorithm simulates the following experimental procedure:

I. An olivine grain containing an inclusion is kept at a given temperature until the inclusion is in complete equilibrium with the host. Within the algorithm, this temperature corresponds to the olivine liquidus temperature of the melt inclusion composition provided (the starting melt composition). The algorithm simulates exchange of Fe and Mg between melt and olivine, which occurs during the re-equilibration process. Re-equilibration may be accompanied by either melting or crystallisation of the host olivine at the inclusion walls.

II. Once equilibrium is reached, the algorithm compares the FeO* content of the melt with the user-specified FeO* content of the trapped melt.

III. If the user-specified FeO* content is higher than the FeO* content of the melt, the algorithm simulates increasing experimental temperature while keeping the melt inclusion and its host in equilibrium. If the user-specified FeO* content is lower than the FeO* content of the melt, the algorithm simulates decreasing experimental temperature while keeping the melt inclusion and its host in equilibrium. In both cases this continues until the FeO* content within the melt inclusion equals the user-specified value. The algorithm simulates melting or crystallisation of olivine and the exchange of Fe and Mg between melt and olivine, which occur during this process.

To use this option, click on the 'Reconstruct MI composition' radio button in the 'Type of Calculations' subsection of the Parameters section of the Main form (Fig. 7.1).

The user must provide the composition of the melt inside the inclusion, the composition of the host olivine (Fo, mol%), and the FeO* content of the trapped melt. These parameters are set within the 'Reconstructing MI composition to a given FeO* content of the trapped melt' subsection of the Parameters section of the Main form (Fig. 7.1).

Note: The data file must include columns that contain the host olivine composition and the FeO* content of the trapped melt for each analysis, if the 'Calculate all analyses from the file' option is used. The column names for these two parameters should read 'Fo_h' and 'FeO_final', respectively (not case sensitive).

User-specified calculation parameters for this option include: olivine-melt equilibrium model; melt oxidation state, model for calculating melt density, and a model for calculating minor element contents (Ca, Mn, Cr) in olivine. The first three parameters are set in the exactly the same way as described in Section 4 of this manual. The last parameter allows the user to introduce minor elements into the calculated olivine composition. The contents of these elements are calculated as a function of olivine Fo content, and are set to typical values for either komatiites, or high-Ca boninites, or MORB / BABB. If the contents of these elements in olivine are set to 0 (None), they are modelled as perfectly incompatible elements.

Note: All calculations within this option are performed at a pressure of 1 atm.

During calculations, Petrolog4 records intermediate output in the Output section of the Main form. This output is provided mainly to keep the user informed of the progress of calculations. Petrolog4 writes the results of calculations into output files.

Note: The reconstructed inclusion composition is automatically copied in the 'Model diffusion profiles' subsection of the Parameters section to be used in modelling diffusion profiles if required.

7.1.1. Saving and loading calculation parameters and structure of output files

Saving and loading calculation parameters is done in the same way as for Crystallisation calculations (see section 4.2).

During reconstructing melt inclusion composition calculations, Petrolog4 saves the following files:

FileName_IRL_calc_param.csv file lists values of all calculation parameters.

FileName_IRS.csv file contains the main output.

For each inclusion, Petrolog4 writes three lines into the output file. The first line, marked by value '1' in the 'No.' column, corresponds to the starting composition. The second line, marked by value '2' in the 'No.' column, corresponds to the moment when inclusion reaches equilibrium with the host (end of step 1 above). The third line, marked by value '3' in the 'No.' column, corresponds to the result of the calculations, when inclusion is in equilibrium with the host and the FeO* in the melt matches the user-defined value.

Values in the 'CORR_COEF' column in the output file should be used to calculate the weight concentrations of perfectly incompatible elements in the recalculated inclusion compositions, by multiplying the values in the starting composition by this coefficient. The values in the 'OL_PER' and 'MELT_PER' columns show weight fractions of olivine and the starting melt during calculations (negative values in the 'OL_PER' column indicate melting of olivine from the walls). These values do not represent the final weight percent change to the starting composition, as inclusions are modelled as open systems to allow for Fe/Mg inter-diffusion during calculations.

Note: When exporting results of previous calculations to Excel, the user must click on the FileName_IRL.csv file to initiate export.

7.2. Modelling diffusive re-equilibration during 'Fe-loss'

Known values of the diffusion coefficient for Fe-Mg inter-diffusion ($D_{\text{Fe-Mg}}$) in olivine allow calculation of the time required for re-equilibration to occur. If an inclusion is completely re-equilibrated, it is possible to calculate the minimum time that the host phenocryst spent at temperatures between trapping and diffusion closure. However, if re-equilibration is not complete when the closure temperature is reached, and thus a diffusion profile around the inclusion is preserved, a quantitative time estimate can be made.

Note: This technique does not allow an estimate of the residence time at (or close to) the trapping temperature, since at these conditions there is no (or very little) crystallisation within the inclusion.

Petrolog4 uses the data from Chakraborty (1997) to calculate the value of $D_{\text{Fe-Mg}}$:

$\text{Lg}(D_{\text{FeMg}}) = -10757/T(\text{K}) - 9.9453 + 0.8063/\text{Fo}$, in sec/m^2 , where Fo for is $(\text{Mg}/(\text{Fe}+\text{Mg}))$ in olivine.

Petrolog4 offers an option for forward modelling of the re-equilibration process during cooling after entrapment (i.e., for the case of 'Fe-loss'). To choose this option, press the 'Model diffusion profile' radio button in the 'Type of Calculations' subsection of the Parameters section of the Main form (Fig. 7.2).

The user must provide the trapped inclusion composition, the inclusion radius (microns) and the length of the cooling interval (in °C). These parameters are set within the 'Model diffusion profiles' subsection of the Parameters section of the Main form (Fig. 7.2).

Note: In this option, the starting composition cannot be imported from a data file.

User-specified calculation parameters for this option include: olivine-melt equilibrium model; melt oxidation state, model for calculating melt density, Fe-Mg inter-exchange diffusion model, and a model for calculating minor element contents (Ca, Mn, Cr) in olivine. The first three parameters are set in the exactly the same way as described in Section 2 of this manual. The last parameter allows the user to introduce minor elements into the calculated olivine composition. The contents of these elements are calculated as a function of olivine Fo content, and are set to typical values for either komatiites, or high-Ca boninites, or MORB / BABB. If the contents of these elements in olivine are set to 0, they are modelled as perfectly incompatible elements.

Note: All calculations within this option are performed at a pressure of 1 atm.

Diffusion modelling can be performed either for the case of instant cooling, or for the case of cooling with a specific cooling rate.

Petrolog 4.0.4 Input from: C:\Programs\PETROLOG\Current_data_File.csv

File Export to MS Excel Tools Help

Crystallisation Reverse Crystallisation Melt Liquidus Association Olivine MI

Type of Calculations:

☐ Reconstruct MI composition
☒ Model diffusion profiles

Ol-melt model: [Herzberg O'Hara 2002](#) Oxidation state: [Oxygen Buffer: 'QFM'](#)
Density model: [Lange & Carmichael 1987](#) Fe-Mg diff. model: [Chakraborty 1997](#)

Set of minor elements (Ca, Mn, Cr) in Olivine
☒ None ☐ High-Ca boninites
☐ Komatiites ☐ MORB or BABB

Reconstructing MI composition to a given FeO* content in the trapped melt

Host olivine composition, Fo: %
FeO* content in the trapped melt: wt. %

☐ Calculate all analyses from the file [Select another analysis](#) [Set volatile and trace elements*](#)

Model diffusion profiles

Starting melt composition

SiO2	TiO2	Al2O3	Fe2O3	FeO	MnO	MgO	CaO	Na2O	K2O	P2O5	Cr2O3	H2O
51.88	1.11	15.65	0.89	6.19	0.16	7.47	10.03	2.24	0.22	0.25	0.09	3.35

Analysis1 ☐ Load the result of the last calculation

Type of calculations:

☒ Instant cooling:
(final % of re-equilibration)

☐ Cooling Rate:
(°C/day)

Inclusion radius, microns:
Cooling interval, °C:
☒ Simulate reheating experiment: T exp (°C)

Output to: Petrolog_Output_*.csv D values: loaded from Current_D_set.PtParamSet
Parameters: last loaded from Current_Param.PtParam modified

Start calculations Clear Results Follow output: On

Modelling diffusion profiles around MI in olivine. Instant cooling

The model used for Olv is: Herzberg & O'Hara 2002
Choice for minor elements in olivine (Ca Mn Cr) is: all set to 0
Fe2O3 in the melt is calculated using QFM buffer of oxygen fugacity
following the model of Borisov et al 2018
SO3 in the melt is calculated using the model of Jugo 2009
Calculation Pressure = 1 atm
Melt density is calculated following the model of Lange & Carmichael 1987
Ds for Olivine:

Mineral	H2O	CO2	S	SO3	Cl	Co	Ni	Rb	Sr	Ba
Olv	0	0	0	0	0	Beatt91	Herzb02	0.001	0.01	0

Cooling interval: 100.00 °C
Extent of re-equilibration: 50.00 %
Inclusion radius: 150.00 micron
Modelling reheating experiment to: 1193.1 °C

***** Warning!!! *****
The chosen olivine model does not incorporate the effect of H2O
and no correction for H2O has been set.

Start instant cooling calculations

Trapping temperature: 1185,

12:00:00 AM sec

Figure 7.2. ‘Olivine MI’ option of Petrolog4 interface for modelling diffusion profiles around melt inclusions.

7.2.1. Instant cooling calculations

In the case of instant cooling, the zoned rim on the walls of the inclusion grows first and then re-equilibration occurs while the grain resides at the lower end of the cooling interval. To use this option, click on the ‘Instant cooling’ radio button in the ‘Type of calculations’ subsection within the ‘Model diffusion profiles’ subsection in the Parameters section of the Main form (Fig. 7.2). For this option, the user needs to specify the extent of re-equilibration, a parameter that will be used to determine when diffusion calculations are completed. This parameter is set in the text box next to the ‘Instant cooling’ radio button. The degree of re-equilibration, i.e., the extent of ‘Fe-loss’, is defined as the amount of FeO* ‘lost’ by the residual melt relative to the amount that is ‘lost’ in the case of complete re-equilibration.

The output file generated within this option contains the melt compositions and diffusion profiles generated at different stages of calculations. The diffusion profiles are expressed as values of FeO* concentration in olivine over distance from the centre of the melt inclusion. The melt compositions recorded correspond to: 1) the starting composition, 2) the composition of the melt after instant cooling (0% re-equilibration), the composition of the melt in the case of complete re-equilibration (100%), and the composition of the melt at the required extent of re-equilibration. The FeO* profiles recorded correspond to the initial rim profile after the instant cooling, and to the resultant FeO* profile after the calculations are completed.

7.2.2. Cooling rate calculations

In the case of cooling with a specific cooling rate, re-equilibration and cooling occur simultaneously. To use this option, click on the ‘Cooling Rate’ radio button in the ‘Type of calculations’ subsection within the ‘Model diffusion profiles’ subsection in the Parameters section of the Main form (Fig. 7.2). For this option,

the user needs to specify the cooling rate, and the calculations will simulate cooling with the specified rate from the start to the end of the cooling interval. This parameter is set in the text box next to the 'Cooling Rate' radio button.

Modelling of diffusion under this option is performed in 10 °C steps, with each step modelled as a separate instant cooling calculation. The program generates two output files. One file contains a record of diffusion profiles at the end of each 10-degree step, and the second file contains melt compositions at the end of each step. 'PR' at the end of the file name denotes files containing calculated FeO profiles. 'COMP' at the end of the file name denotes files containing calculated melt compositions.

7.2.3. Modelling complex cooling histories

To enable modelling of complex cooling histories, Petrolog4 allows for using the result of the last calculation as the starting point for the next calculation. For this purpose, after each diffusion modelling calculation Petrolog4 saves both the final profile and the final melt composition into a file called 'LAST_RES.DAT'. In order to use the results of the last calculation as the starting point for the following calculation, check the 'Load last result' checkbox in the 'Diffusion profiles modelling' part of the Parameters section of the Main form (Fig. 4.16).

Note: Loading the results of the last calculation automatically sets the size for the inclusion radius, which should not be changed.

Note: It is recommended that the user does not delete file 'LAST_RES.DAT' from the directory which contains the Petrolog4 executable (i.e., 'Petrolog.exe' file).

7.2.4. Simulating reheating experiments

Calculation under both Instant cooling and Cooling rate options can simulate a reheating experiment with the melt inclusions, an optional calculation performed at the end of diffusions modelling. To include this calculation, check the 'Simulate reheating experiment' checkbox within the 'Model diffusion profiles' subsection in the Parameters section of the Main form (Fig. 7.2). The user is then also required to provide a temperature value for the reheating experiment. The temperature is set in the 'T exp (°C)' text box next to the 'Simulate reheating experiment' checkbox.

Using this option allows Petrolog4 to reproduce the following scenario: 1) inclusion is trapped; 2) after entrapment, inclusion is cooled within the plumbing system prior to eruption; 3) the grain with the inclusion is experimentally reheated to a certain temperature and quenched. The results of diffusion modelling can then be directly compared with the analysed composition of the experimentally quenched inclusion.

Note: If the results of a diffusion modelling calculation are intended to be used in the following calculation, simulation of the reheating experiment should not be performed.

7.2.5. Integrating reconstruction of inclusion compositions and diffusion modelling

To facilitate combining calculations of the initial trapped inclusion compositions with diffusion modelling, Petrolog4 populates the Starting melt composition for the 'Model diffusion profiles' option with the result of the calculation performed with the 'Reconstructing MI composition to a given FeO* value' option. Temperature value for experimental reheating is also set to correspond to the olivine liquidus temperature of the starting composition for the 'Reconstructing MI composition to a given FeO* content in the trapped melt'.

Note: It is recommended that the user contact Petrolog support if advanced use of the diffusion modelling is intended.

References

- Almeev RR, Holtz F, Koepke J, Fleurice P, Botcharnikov RE 2007. The effect of H₂O on olivine crystallization in MORB: Experimental calibration at 200 MPa. *Amer. Mineral.* 92, 670-674.
- Almeev RR, Holtz F, Koepke J, Fleurice P 2012. Experimental calibration of the effect of H₂O on plagioclase crystallization in basaltic melt at 200 MPa. *Amer. Mineral.* 97, 1234-1240.
- Ariskin AA, Barmina GS 1990. Equilibria thermometry between plagioclases and basalt and andesite magmas. *Geochem. Int.* 27(10), 129-134.
- Ariskin AA, Barmina GS 1999. An empirical model for the calculation of spinel-melt equilibria in mafic igneous systems at atmospheric pressure: 2. Fe-Ti oxides. *Contrib. Mineral. Petrol.* 134, 251-263.
- Ariskin AA, Barmina GS, Frenkel MYa 1986. Simulating low-pressure tholeiite-magma crystallization at a fixed oxygen fugacity. *Geokhimiya*, No. 11, 1614-1627; translated into English in *Geochem. Int.* 1987, 24(5), 92-100.
- Ariskin AA, Frenkel MYa, Barmina GS, Nielsen R 1993. COMAGMAT: a Fortran program to model magma differentiation processes. *Comput. Geosci.* 19, 1155-1170.
- Ariskin AA, Nikolaev GS 1996. An empirical model for the calculation of spinel-melt equilibria in mafic igneous systems at atmospheric pressure: 1. Chromian spinels. *Contrib. Mineral. Petrol.* 123, 282-292.
- Beattie P 1993. Olivine-melt and orthopyroxene-melt equilibria. *Contrib. Mineral. Petrol.* 115, 103-111.
- Beattie P, Ford C, Russell D 1991. Partition-Coefficients For Olivine-Melt And Ortho-Pyroxene-Melt Systems. *Contributions to Mineralogy and Petrology* 109, 212-224.
- Blundy JD, Wood BJ 1991. Crystal-chemical controls on the partitioning of Sr and Ba between plagioclase feldspar, silicate melts, and hydrothermal solutions. *Geochim Cosmochim Acta* 55, 193-209.
- Bolikhovskaya SV, Vasil'eva MO, Koptev-Dvornikov EV 1996. Simulating low-Ca pyroxene crystallization in basic systems: new versions of geothermometers. *Geochem. Int.* 33 (12), 1-19.
- Borisov AA, Shapkin AI 1990. A new empirical equation rating Fe³⁺/Fe²⁺ in magmas to their composition, oxygen fugacity, and temperature. *Geochem. Int.* 27, 111-116.
- Borisov A, Behrens H, Holtz F 2018. Ferric/ferrous ratio in silicate melts: a new model for 1 atm data with special emphasis on the effects of melt composition. *Contrib. Mineral. Petrol.* 173, 98.
- Bottinga Y, Weill DF 1972. The viscosity of magmatic silicate liquids: a model for calculation. *Amer. J. Sci.* 272, 438-475.
- Bychkov D.A. CryMinal program and a set of composimeters: tools for modeling equilibria between silicate melts and minerals (in Russian) Ph. D. thesis. Moscow, 2023, 139pp., available at: <https://dissovet.msu.ru/download/f2692eec-f3b4-11ed-87b7-005056b96f20>
- Chakraborty S 1997. Rates and mechanisms of Fe-Mg interdiffusion in olivine at 980°-1300°. *Journal of Geophysical Research-Solid Earth* 102, 12317-12331.
- Danyushevsky LV 2001. The effect of small amounts of H₂O on crystallisation of mid-ocean ridge and backarc basin magmas. *J. Volcan. Geoth. Res.* 110, 265-280.
- Danyushevsky LV, Della-Pasqua FN, Sokolov S 2000a. Re-equilibration of melt inclusions trapped by magnesian olivine phenocrysts from subduction-related magmas: petrological implications. *Contrib. Mineral. Petrol.* 138, No.1, 68-83.
- Danyushevsky LV, Plechov P 2011. Petrolog3: Integrated software for modeling crystallization processes. *Geochem. Geophys. Geosyst.* 12, Q07021.
- Danyushevsky LV, Sokolov S, Falloon TJ 2002: Melt inclusions in olivine phenocrysts: using diffusive re-equilibration to determine the cooling history of a crystal, with implications for the origin of olivine-phyric volcanic rocks. *J. Petrology* 43, 1651-1671.
- Ding S, Plank T, Wallace PJ, Rasmussen DJ 2023. Sulfur_X: A Model of Sulfur Degassing During Magma Ascent. *Geochem. Geophys. Geosyst.* 24, e2022GC010552. <https://doi.org/10.1029/2022GC010552>
- Drake MJ 1976. Plagioclase-melt equilibria. *Geochim. Cosmochim. Acta* 40, 457-465.
- Falloon TJ, Danyushevsky, LV 2000. Melting of refractory mantle at 1.5, 2.0 and 2.5 GPa under H₂O-undersaturated conditions: implications for the petrogenesis of high-Ca boninites and the influence of subduction components on mantle melting. *J. Petrology* 41, 257-283.

- Ford CE, Russell DG, Groven JA, Fisk MR 1983. Distribution coefficients of Mg^{2+} , Fe^{2+} , Ca^{2+} and Mn^{2+} between olivine and melt. *J. Petrol.* 24, 256-265.
- Fortin MA, Riddle J, Desjardins-Langlais Y, Baker DR 2015. The effect of water on the sulfur concentration at sulfide saturation (SCSS) in natural melts. *Geochim Cosmochim Acta* 160, 100-116.
- Gaetani GA, Watson EB 2002. Modelling the major-element evolution of olivine-hosted melt inclusions. *Chem. Geology* 183, 25-41.
- Giordano D, Dingwell DB 2003. Non-Arrhenian multicomponent melt viscosity: a model. *Earth and Planetary Science Letters* 208, 337-349.
- Herzberg C, O'Hara MJ 2002. Plume-associated ultramafic magmas of phanerozoic age. *J. Petrol.* 43, 1857-1883.
- Iacono-Marziano G, Morizet Y, Le Trong E, Gaillard F 2012. New experimental data and semi-empirical parameterization of H_2O - CO_2 solubility in mafic melts. *Geochim. Cosmochim. Acta* 97, 1-22.
- Jugo PJ 2009. Sulfur content at sulfide saturation in oxidized magmas. *Geology* 37, 415-418.
- Kilinc A, Carmichael ISE, Rivers ML, Sack RO 1983. The ferric-ferrous ratio of natural silicate liquids equilibrated in air. *Contrib. Mineral. Petrol.* 83, 136-140.
- Kinzler RJ, Grove TL, Recca SI 1990. An Experimental-Study On The Effect Of Temperature And Melt Composition On The Partitioning Of Nickel Between Olivine And Silicate Melt. *Geochim Cosmochim. Acta* 54, 1255-1265.
- Kiseeva ES, Wood BJ 2015. The effects of composition and temperature on chalcophile and lithophile element partitioning into magmatic sulphides. *Earth and Planetary Science Letters* 424, 280-294.
- Koshlyakova AN, Sobolev AV, Krashenninnikov SP, Batanova VG, Borisov AA 2022. Ni partitioning between olivine and highly alkaline melts: An experimental study. *Chem. Geology* 587, 120615. <https://doi.org/10.1016/j.chemgeo.2021.120615>.
- Kress VC, Carmichael ISE 1988. Stoichiometry of the iron oxidation reaction in silicate melts. *Amer. Mineral.* 73, 1267-1274.
- Kress VC, Carmichael ISE 1991. The compressibility of silicate liquids containing Fe_2O_3 and the effect of composition, temperature, oxygen fugacity and pressure on their redox states. *Contrib. Mineral. Petrol.* 108 82-92.
- Lange RA, Carmichael ISE 1987. Densities of Na_2O - K_2O - CaO - MgO - FeO - Fe_2O_3 - Al_2O_3 - TiO_2 - SiO_2 liquids: New measurements and derived partial molar properties. *Geochim. Cosmochim. Acta* 51, 2931-2946.
- Langmuir CH, Klein EM, Plank T 1992. Petrological systematics of Mid-Ocean Ridge Basalts: Constraints on melt generation beneath ocean ridges. In: *Mantle flow and melt generation at mid-ocean ridges*. AGU Geophysical Monograph 71, pp. 183-280.
- Li C, Ripley EM 2005 Empirical equations to predict the sulfur content of mafic magmas at sulfide saturation and applications to magmatic sulfide deposits. *Mineralium Deposita* 40, 218-230.
- Li C, Ripley EM 2009 Sulfur Contents at Sulfide-Liquid or Anhydrite Saturation in Silicate Melts: Empirical Equations and Example Applications. *Econom. Geol.* 104, 405-412.
- Lindsley DH (ed) 1991. *Oxide Minerals: Petrologic and Magnetic Significance*. Reviews in Mineralogy, v. 25.
- Medard E, Grove TL 2008. The effect of H_2O on the olivine liquidus of basaltic melts: Experiments and thermodynamic models. *Contrib. Mineral. Petrol.* 155, 417-432.
- Moore G, Vennemann T, Carmichael ISE 1998. An empirical model for the solubility of H_2O in magmas to 3 kilobars. *American Mineralogist* 83, 36-42.
- Nash WM, Smythe DJ, Wood BJ 2019. Compositional and temperature effects on sulfur speciation and solubility in silicate melts. *Earth and Planetary Science Letters* 507, 187-198.
- Nathan HD, Vankirk CK 1978. A model of magmatic crystallisation. *J. Petrol.* 19, 66-94.
- Newman S, Lowenstern JB 2002. VolatileCalc: a silicate melt- H_2O - CO_2 solution model written in Visual Basic for excel. *Computers and Geosciences* 28, 597-604.
- Nelson SA, Carmichael ISE 1979. Partial Molar Volumes of Oxides Component in Silicate Liquids. *Contrib. Mineral. Petrol.* 71, 117-124.
- Nielsen RL 1985. EQUIL: A program for the modeling of low-pressure differentiation processes in natural mafic magma bodies. *Computers and Geosciences* 11, 531-546.

- Nielsen RL 1988. TRACE.FOR: A program for the calculation of combined major and trace-element liquid lines of descent for natural magmatic systems. *Computers and Geosciences* 14, 15-35.
- Nielsen RL, Drake MJ 1979. Pyroxene-melt equilibria. *Geochim. Cosmochim. Acta* 43, 1259-1272.
- Nielsen RL, Dungan MA 1983. Low pressure mineral-melt equilibria in natural anhydrous mafic systems. *Contrib. Mineral. Petrol.* 84, 310-326.
- O'Neill HStC 2021. The Thermodynamic Controls on Sulfide Saturation in Silicate Melts with Application to Ocean Floor Basalts. *Magma Redox Geochemistry, Geophysical Monograph* 266, 177-213.
- O'Neill HStC, Mavrogenes JA 2022. The sulfate capacities of silicate melts. *Geochim. Cosmochim. Acta* 334, 368-382.
- Pletchov PYu, Gerya TV 1998. Effect of H₂O on plagioclase-melt equilibrium. *Experiment in GeoSciences* 7, No. 2, 7-9.
- Putirka KD 2005. Mantle potential temperatures at Hawaii, Iceland, and the mid-ocean ridge system, as inferred from olivine phenocrysts: Evidence for thermally driven mantle plumes. *Geochem. Geophys. Geosyst.* 6. Q05L08.
- Roeder PL, Emslie RF 1970. Olivine-liquid equilibrium. *Contrib. Mineral. Petrol.* 29, 275-89.
- Sack RO, Carmichael ISE, Rivers ML, Ghiorso MS 1980. Ferric-ferrous equilibria in natural silicate liquids at 1 bar. *Contrib. Mineral. Petrol.* 75, 369-376.
- Smithe DJ, Wood BJ, Kiseeva ES 2017. The S content of silicate melts at sulfide saturation: New experiments and a model incorporating the effects of sulfide composition. *American Mineralogist*, Volume 102, pages 795–803. <http://dx.doi.org/10.2138/am-2017-5800CCBY>
- Sobolev AV, Slutskiy AB 1984. Composition and crystallisation conditions of the initial melt of the Siberian meimechites in relation to the general problem of the ultrabasic magmas. *Soviet Geology and Geophysics* 25, 93-104.
- Toplis MJ 2005. The thermodynamics of iron and magnesium partitioning between olivine and liquid: criteria for assessing and predicting equilibrium in natural and experimental systems. *Contrib. Mineral. Petrol.* 149, 22-39.
- Weaver JS, Langmuir CH 1990. Calculation of phase equilibrium in mineral-melt systems. *Computers and Geosciences* 16, 1-19.

Appendix 1. List of available models

Olivine-melt equilibrium models: Ariskin et al., 1986; Ariskin et al., 1993; Beattie, 1993; Bychkov, 2023; Danyushevsky, 2001; Ford et al., 1983; Gaetani and Watson, 2002; Herzberg and O'Hara, 2002; Langmuir et al., 1992; Nielsen, 1985; Nielsen, 1988; Putirka, 2005; Roeder and Emslie, 1970; Sobolev and Slutskiy, 1984; Weaver and Langmuir, 1990.

Olivine-melt Fe-Mg exchange Kd models: $K_d = \text{const}'$; $\ln(K_d) = A/T(K) + B \cdot P(\text{kbar})/T(K) + C'$; Sobolev and Danyushevsky, 1994; Toplis, 2005.

Plagioclase-melt equilibrium models: Ariskin and Barmina, 1990; Ariskin et al., 1993; Bychkov, 2023; Danyushevsky, 2001; Drake, 1976; Langmuir et al., 1992; Nielsen, 1985; Nielsen and Dungan, 1983; Plechov and Gerya, 1998; Weaver and Langmuir, 1990.

Clinopyroxene-melt equilibrium models: Ariskin et al., 1986; Ariskin et al., 1993; Bychkov, 2023; Danyushevsky, 2001; Langmuir et al., 1992; Nielsen, 1985; Nielsen, 1988; Nielsen and Drake, 1979; Weaver and Langmuir, 1990.

Orthopyroxene-melt equilibrium models: Ariskin et al., 1993; Beattie, 1993; Bolikhovskaya et al., 1995; Bychkov, 2023; Nielsen and Drake, 1979.

Pigeonite-melt equilibrium models: Ariskin et al., 1986; Ariskin et al., 1993; Bolikhovskaya et al., 1995; Bychkov, 2023; Nielsen, 1988.

Spinel-melt equilibrium models: Ariskin and Nikolaev, 1996; Nielsen, 1985.

Ilmenite-melt equilibrium models: Ariskin and Barmina, 1999; Nielsen, 1985.

Magnetite-melt equilibrium models: Ariskin and Barmina, 1999.

Sulphide melt- silicate melt equilibrium models: Kiseeva and Wood, 2015; O'Neill, 2021; pure FeS.

Fluid-melt equilibrium models: Iacono-Marziano et al., 2012; Newman and Lowenstern, 2002 (VolatileCalc); pure H₂O.

Models for setting H₂O corrections to calculated temperatures:

Olivine: Almeev et al., 2007; Danyushevsky, 2001; Medard and Grove, 2008;

Plagioclase: Almeev et al., 2012; Danyushevsky, 2001.

Sulphur saturation models: Li and Ripley, 2005; Li and Ripley, 2009; Fortin et al., 2015; O'Neill, 2021; Smythe et al., 2017.

Fluid saturation models: Iacono-Marziano et al., 2012; Moore et al., 1998; Newman and Lowenstern, 2002.

Models of Fe oxidation state in the melt: Borisov and Shapkin, 1990; Borisov et al., 2018; Kilinc et al., 1983; Kress and Carmichael, 1988; Kress and Carmichael, 1991; Sack et al., 1980.

Models of S oxidation state in the melt: Jugo 2009; Nash et al., 2019; O'Neill HStC and Mavrogenes, 2022.

Melt density models: Lange and Carmichael, 1997; Nelson and Carmichael, 1979

Melt viscosity models: Bottinga and Weill, 1972 and Giordano and Dingwell, 2003.

Models for trace element distribution coefficients between a phase and the silicate melt:

Olivine: Beattie et al., 1991 (Ni and Co); Kinzler et al., 1990 (Ni); Koshlyakova et al., 2022 (Ni);

Plagioclase: Blundy and Wood, 1991 (Ba and Sr)

Fluid: Ding et al., 2023 (S²⁻ and S⁶⁺).

Oxygen buffers:

$\lg fO_2 = A / TK + B + C * (P_{bar}-1) / TK$			
Buffer	A	B	C
QFe	-29520.8	7.492	0.05
Fe-W	-27489	6.702	0.055
WM	-32807	13.012	0.083
Co-CoO	-24332.6	7.295	0.052
QFM	-25096.3	8.735	0.11
Ni-NiO	-24930	9.36	0.046
MH	-25700.6	14.558	0.019